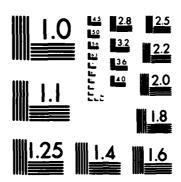
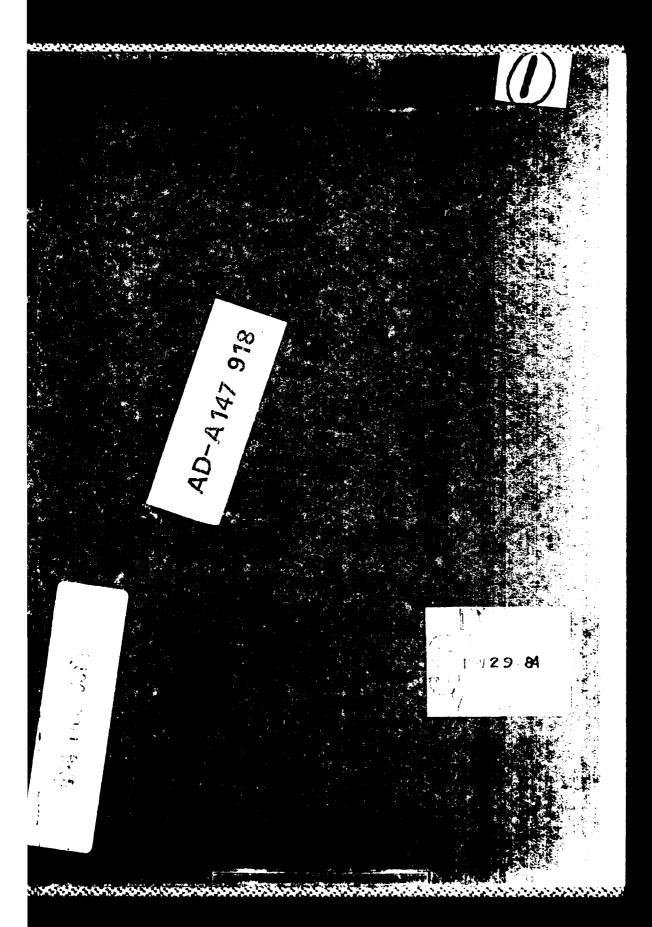
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ABSTRACT

Author: Thomas Joseph Walker, Major, USAF, RSC

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Trichloroethylene (TCE) is a widely detected contaminant in groundwater. This study investigated fate of TCE in two similar soils with differing organic carbon contents. TCE was applied to soil columns in one 5 or 10 ml quantity, then eluted with 50 or 100 ml of water/day.

The 1.4% organic carbon soil retarded TCE elution more than did the 0.53% soil. Column effluent TCE reached 840-1,100 mg/l with the 0.53% organic carbon soil having higher TCE concentrations. For columns subjected to 10 ml TCE, effluent TCE remained constant at approximately 1,100 mg/l until 50-60% of applied TCE was eluted. Water application rate had no measurable effect on elution.

Batch isotherms for both soils and two particle sizes (fine, < 0.150 mm; coarse, < 2 mm) paralleled Freundlich theory.

Adsorptive capacity increased with increased organic carbon content and decreased particle size. Based on normalized organic carbon content, adsorption was dependent upon inorganic surface area.

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Complies with University regulations and meets the standards of originality and quality	the Graduate School for
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FATE AND DISPOSITION OF TRICHLOROETHYLENE

IN SURFACE SOILS

A Thesis
Submitted to the Faculty
of
Purdue University

by
Thomas Joseph Walker

In Partial Fulfillment of the
Requirements for the Degree

of

Doctor of Philosophy

August 1984

To Jane, Jenny, Rachel, and Kate - your love made this possible.

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	Хi
ABSTRACT	xiv
INTRODUCTION	1
LITERATURE REVIEW	4
TCE Manufacture and Use Properties of TCE Health Aspects of TCE TCE Occurrence in Groundwater Soil Environment Chemical Transport in Soil Degradation Summary	4 7 9 12 15 21 51
MATERIALS AND METHODS	61
Description of Soils	61 63 64 66 67 78 82
PRELIMINARY INVESTIGATIONS	85
Soil Analyses	85 89 94 99 102 105

TABLE OF CONTENTS, Continued

	Page
RESULTS AND DISCUSSION	112
Batch Adsorption Studies	112 132 174 179 206 208
SUMMARY	217
CONCLUSIONS AND RECOMMENDATIONS	225
Conclusions	225 2 27
LIST OF REFERENCES	229
APPENDICES	
Appendix A. Sample Calculations Appendix B. Tabulated Data from Soil	239
Column Studies Appendix C. Tabulated Data from TCE:Soil Adsorption Studies	243 330
Appendix D. Tabulated Data from TCE:Soil Warburg Respirometry	
Studies	335
VITA	350

LIST OF TABLES

Table	e 1	Page
1.	Recent Annual TCE Production	5
2.	Physical Properties of TCE	5
3.	TCE Nomenclature and Identity Information	8
4.	Synthetic Organic Chemicals Most Commonly Found in Groundwater (92)	13
5.	Occurrence of TCE in Drinking Water (92)	13
6.	Projected Cancer Risks for Drinking Water Concentrations of TCE (92)	16
7.	Variation in Concentration of Microorganisms with Depth for a Typical Mineral Soil (1)	16
8.	Particle Size Information from Representative Soil Adsorption Studies	37
9.	Reported Equilibration Times for Batch Isotherm Studies	39
10.	Parameters from Packed Column Adsorption Studies	41
11.	Summary of Data from Packed Column Study (77)	42
12.	Analyses Conducted by the Soil Characterization Laboratory	n 65
13.	GC Linearity Data for Headspace Analysis	73
14.	TCE Recovery from Composite Soil Samples	78
15.	CEC, Organic Carbon, Particle Size Distribution, and pH of Soils	86
16.	Physical Parameters of Soils	87

Table	e	Page
17.	Calculated Soil and Organic Carbon Mass	88
18.	Loss of TCE through Pierced Septa	100
19.	Variation in FID Response Due to Sample Matrix	100
20.	Variation in FID Response with Sample Volume.	103
21.	Calculated TCE Adsorption	106
22.	Operating Conditions for Column Soil Studies.	110
23.	Summary of Experimental Values Used to Determine Soil Adsorption Isotherms for TCE	114
24.	Freundlich Constants Determined from Equilibrium Adsorption Isotherms for TCE Applied to Soils	115
25.	Calculated X/M Values for Various TCE Concentrations	115
26.	Data from Time of Adsorption Experiment for Chalmers Soil Subjected to TCE Application	122
27.	Data from Time of Adsorption Experiment for Russell Soil Subjected to TCE Application	124
28.	Summary of Data from Glass Adsorption Study with TCE	129
29.	Summary of Data from Gravel Adsorption Study with TCE	129
30.	Mean, Standard Deviation, and Range of Daily Volume of Effluent Collected from Chalmers Soil Columns	134
31.	Mean, Standard Deviation, and Range of Daily Volume of Effluent Collected from Russell Soil Columns	136
32.	Maximum, Minimum, and Mean pH for Soil Column Effluents	160
33.	Summary of Soil Column Effluent Chloride Measurements	183

Table	e	Page
34.	Total Oxygen Uptake from Acclimated Soil Warburg Studies When Supplemented with TCE or Glucose	192
35.	Percent Substrate Respired from Acclimated Soil Warburg Studies When Supplemented with TCE or Glucose	193
36.	Rate of TCE Respiration from Acclimated Soil Warburg Studies When Supplemented with TCE	194
37.	Rate of Endogenous Respiration and Carbon Dioxide Production for Soil Samples from Columns at Various Depths	203
38.	TCE Eluted in Soil Column Effluents	209
39.	Concentration and Mass of TCE Remaining on Soil Columns After Elution	212
40.	TCE Mass Balance for Soil Columns Operated Continuously with Water Application for 132 Consecutive Days	214
Apper Table		
B1.	Cross Reference of Column Study Day with Calendar Date	244
B2.	Daily Data for Columns Cl, C2, and C3	245
в3.	Daily Data for Columns C4, C5, and C6	254
B4.	Daily Data for Columns C7, C8, and C9	263
B5.	Daily Data for Columns Cl0, Cl1, and Cl2	271
В6.	Daily Effluent Volume from Chalmers Soil Control Column	280
в7.	Daily Data for Columns R1, R2, and R3	282
в8.	Daily Data for Columns R4, R5, and R6	291
в9.	Daily Data for Columns R7, R8, and R9	300
B10.	Daily Data for Columns R10. R11. and R12	309

Table		Page
B11.	Daily Effluent Volume from Russell Soil Control Column	318
B12.	TCE Time of Saturation	320
в13.	pH of Chalmers Soil Column Effluent	321
B14.	pH of Russell Soil Column Effluent	322
B15.	Effluent Volume and TCE Concentrations Used to Determine TCE Eluted from Columns by Simpson's Approximation	323
B16.	Cumulative Mass of TCE Eluted from Chalmers Soil Columns	324
B17.	Cumulative Mass of TCE Eluted from Russell Soil Columns	325
B18.	Cumulative Mass of TCE Eluted Based Upon Comparison to a CSTR (53)	326
B19.	Ammonia Concentrations in Soil Column Effluents	327
B20.	Nitrate Concentrations in Soil Column Effluents	328
B21.	Chloride Concentrations in Soil Column Effluents	329
C1.	Data for Determination of Soil Adsorption Isotherms	331
C2.	Data for Determination of X/M Values in Time of Adsorption Experiment	332
C3.	Data for Determination of Glass Adsorption Isotherm	334
C4.	Data for Determination of Gravel Adsorption Isotherm	334
Dl.	Warburg Data for Unacclimated Chalmers Soil Supplemented with TCE from 2.5 Inch Depth	336
D2.	Warburg Data for Acclimated Chalmers Soil Supplemented with TCE from 2.5 Inch Depth	338

Tab	le		Page
D3.		for Acclimated Chalmers Soil with TCE from 15 Inch Depth	340
D4.		for Acclimated Chalmers Soil with TCE from 31 Inch Depth	342
D5.	-	for Acclimated Russell Soil with TCE from 2.5 Inch Depth	344
D6.	_	for Acclimated Russell Soil with TCE from 15 Inch Depth	346
D7.	_	for Acclimated Russell Soil with TCE from 31 Inch Depth	348



LIST OF FIGURES

Figu	re	Page
1.	Possible Routes of Reductive Dechlorination (46)	58
2.	GC Response for Different Sample Volumes	74
3.	Diagram of Soil Column	90
4.	Extrusion of Soil Core Into Column	92
5.	Collection of Sample without TCE Analysis	95
6.	Collection of Sample with TCE Anlaysis	9 5
7.	Variation in FID Response with Different Sample Volumes	104
8.	Column Study Assembly	1.08
9.	TCE Adsorption Isotherm for Composite Mixture of Chalmers Soil	116
10.	TCE Adsorption Isotherm for Composite Mixture of Russell Soil	117
11.	Adsorption Equilibration for Coarse Particle Soil with TCE Concentration of 220 mg/l	126
12.	Adsorption Equilibration for Coarse Particle Soil with TCE Concentration of 880 mg/l	126
13.	Adsorption Equilibration for Fine Particle Soil with TCE Concentration of 220 mg/l	127
14.	Adsorption Equilibration for Fine Particle Soil with TCE Concentration of 880 mg/l	127
15.	Composite TCE Elution Curve: Chalmers Soil Columns Cl, C2, and C3	141

LIST OF FIGURES, Continued

Figu	re	Page
16.	Composite TCE Elution Curve: Chalmers Soil Columns C4, C5, and C6	142
17.	Composite TCE Elution Curve: Chalmers Soil Columns C7, C8, and C9	143
18.	Composite TCE Elution Curve: Chalmers Soil Columns ClO, Cll, and Cl2	144
19.	Composite TCE Elution Curve: Russell Soil Columns Rl, R2, and R3	145
20.	Composite TCE Elution Curve: Russell Soil Columns R4, R5, and R6	146
21.	Composite TCE Elution Curve: Russell Soil Columns R7, R8, and R9	147
22.	Composite TCE Elution Curve: Russell Soil Columns R10, R11, and R12	148
23.	Time of Saturation for TCE and Water	159
24.	Composite TCE Elution Curves for 5 ml TCE Application to Soil Columns	162
25.	Composite TCE Elution Curves for 10 ml TCE Application to Soil Columns	163
26.	Composite TCE Elution Curves for 50 ml/day Water Application Rate to Soil Columns	164
27.	Composite TCE Elution Curves for 100 ml/day Water Application Rate to Soil Columns	165
28.	Composite TCE Elution Curves for Chalmers Soil Columns	166
29.	Composite TCE Elution Curves for Russell Soil Columns	167
30.	Cumulative Mass Elution of TCE from Soil Columns	176
31.	Cumulative Percentage Elution of TCE from Soil Columns	177

LIST OF FIGURES, Continued

Fig	ure	Page
32.	Warburg Oxygen Uptake for Unacclimated Chalmers Soil Supplemented with TCE for 2.5 Inch Depth	186
33.	Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 2.5 Inch Depth	189
34.	Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with a Glucose Substrate	190
35.	Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 15 Inch Depth.	196
36.	Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 31 Inch Depth.	197
37.	Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 2.5 Inch Depth	198
38.	Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 15 Inch Depth.	199
39.	Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 31 Inch Depth.	200
40.	Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with a Glucose Substrate.	201

ABSTRACT

رهوا برهانه والبراق كرون ويمهر توسيكه في تبدير ويناه كالمدين كالمراب بالمراب المرك المواقي المواقي المراب المرابي المرابي

Walker, Thomas Joseph. Ph.D., Purdue University, August 1984. Fate and Disposition of Trichloroethylene in Surface Soils. Major Professor: Dr. James E. Etzel.

Trichloroethylene (TCE) is widely detected as a contaminant in groundwater due to discharges or spills. This study investigated the fate of TCE in two similar soils with differing organic carbon contents. TCE was applied to soil columns in one 5 or 10 ml quantity, then eluted over 132 consecutive days with 50 or 100 ml of water/day.

The 1.4% organic carbon soil retarded elution of TCE more than did the 0.53% soil. Column effluent TCE reached 840-1,100 mg/l with the 0.53% organic carbon soil having higher TCE concentrations. For columns subjected to 10 ml TCE, effluent TCE remained constant at approximately 1,100 mg/l until 50-60% of applied TCE was eluted. Water application rate had no measurable effect on elution.

Batch isotherms for both soils and two particle sizes (fine, < 0.150 mm; coarse, < 2 mm) paralleled the Freundlich theory. Adsorptive capacity increased with increased organic carbon content and decreased particle size. Based on normalized organic carbon content, adsorption was found to be dependent upon inorganic surface area. Equilibration

time studies for 220-880 mg/l TCE showed adsorption to be complete within 20 hours.

Biodegradation of TCE in the soils, based on effluent TCE and chlorides, was not enhanced by addition of ammonia to elution water. Warburg studies showed TCE was inhibitory to biological activity at concentrations of 55-1,100 mg/l in unacclimated soil. Acclimated soil of both types from 2.5 and 15 inch depths showed degradation of TCE at 55 mg/l but not 110 or 550 mg/l. Addition of ammonia enhanced mass of TCE respired but not respiration rate. No evidence of cis or trans-1,2-dichloroethylene was found in column effluents. In all, degradation (biological and abiotic) accounted for 0.3% or less of TCE.

A mass balance indicated TCE retention in the soil directly correlated with soil organic carbon content. Elution and volatilization were major sinks for TCE. Volatilization accounted for 15.6-32.8% of TCE applied.

INTRODUCTION

Groundwater serves many individuals and municipalities throughout the United States, with estimates that 40-50% of our population depend upon it as a drinking water source (36,57). In most locations, groundwater has been and will continue to be a reliable and healthful source of water.

Recent evidence, though, has indicated that much of the groundwater within the country, particularly in urban and industrial areas, may be contaminated with anthropogenic organic chemicals. Presence of some of these chemicals in groundwater poses serious public health problems because of their toxicity. These compounds are usually present in groundwater due to accidental spills or illicit dumping (46).

Environmental regulatory agencies and legislative bodies have recognized the need to control and regulate the entry of hazardous chemicals into the environment. Examples of this control legislation include the Safe Drinking Water Act, the Clean Water Act, Toxic Substance Control Act, and Resource Conservation and Recovery Act (46,51,87,89). While this legislative emphasis has been aimed to reduce or

eliminate the purposeful entry of organics into the environment, discharges of chemicals by spills or illegal release have occurred and will probably continue to occur.

The gravity of the health effects of groundwater contamination is nearly matched by the cost to identify the extent and magnitude of a contaminated zone within an aquifer. Problems are encountered because of the lack of research on the phenomena that control contaminant transport in concentrations that vary over several orders of magnitude (35,36,37). Extensive research has been conducted on the transport of pesticides in the environment. Very little literature, though, has addressed the problems associated with organic contaminant transport, particularly at concentrations in the high mg/l range that would be associated with the release or discharge of a chemical in the environment.

The purpose of this research was to investigate the fate of one particular chemical, trichloroethylene, as introduced to soil columns in a non-solution form such as in a spill or discharge. Subsequent elution of the trichloroethylene with deionized water was used to simulate rainfall. Trichloroethylene was chosen because of its classification as a priority pollutant (89), its widespread use (80), and its frequent occurrence in groundwater (63,74). The soils chosen for this research possessed different organic carbon

contents and represented typical soils commonly found throughout the country.

The literature contains no evidence of comprehensive research on the fate of trichloroethylene in soils, especially at high concentrations. Therefore, the goal of this project was to determine this fate as a result of elution and the adsorptive:desorptive and degradative properties of the soil. An understanding of these factors would allow a better estimate of the necessity or urgency to contain or clean up spills of trichloroethylene on surface soils to prevent groundwater contamination.

LITERATURE REVIEW

In order to properly plan the proposed research investigation on the consequence of an accidental spill of trichloroethylene onto soil, an understanding of why TCE is of concern and how it can be transported in the environment was desirable. Included in this review are the major areas of: manufacture, use, properties; health aspects; groundwater contamination potential; soil environment interactions; and, most extensively, chemical transport in soil. The information on all of these factors was then used to decide the protocol for the research studies.

TCE Manufacture and Use

Trichloroethylene (TCE) is a chemical that has been of important industrial significance since the 1920's. It was first synthesized in Europe in 1864 and patented in 1906 (87,97) but commercial production of TCE in the United States did not begin until 1935 (87). Production is primarily by three chemical companies: Dow Chemicals, Ethyl Corporation, and PPG Industries (80). Recent annual U.S. production figures are listed in Table 1.

Table 1. Recent Annual TCE Production.

Year	Annual Production (million of pounds)	Reference
1970	610	78
1973	452	78
1974	434	78
1975	515	91
1981	365	80

Table 2. Physical Properties of TCE.

Property		Reference
Boiling point, C, (760 mm Hg)	86.7 87.0	45,103 94
Melting point, C	-87.1 -86.8 -73.0	45,103 76 94
Vapor pressure, mm Hg, 20C	57.8 57.9 58.0	45 94 43
<pre>Vapor density, boiling point, l atm, g/liter</pre>	4.45	45
Specific gravity (liquid)	1.46	45
Octanol/Water Partition Coefficient	195	94
Log Octanol/Water Partition Coefficient	2.29	94
Solubility in water, 20C, mg/l	1,100	45,51
Henry's Law Constant, atm-m ³ /mol	11.7x10-	3 96

TCE is commercially produced by two different processes (31,45,97). The most widely used method which accounts for 90% of production, is a dual step process in which acetylene is initially chlorinated to tetrachloroethane in a packed tower at 50°C. The tetrachloroethane is then removed and processed through a dehydroxychlorination step. This can be done by alkaline hydrolysis with calcium hydroxide in water or by thermal decomposition in the presence of an activated charcoal catalyst at 300-500°C. The reactions involved are:

2.
$$C_2H_2Cl_4$$
 \longrightarrow $C1HC$ \longrightarrow $CCl_2 + HCl$

The other process involves oxychlorination of 1,2-dichloroethane:

$$O_2(air) + HC1 + C_2H_4C1_2 \longrightarrow C_2HC1_3 + 2H_2O$$

TCE is used in a variety of ways and in many different products. Approximately 90% of TCE is used as a solvent in liquid or vapor degreasing of metal parts before some type of metal finishing (15,76,87,91). Approximately 5% of TCE is used as a dry cleaning solvent, an extractant in food and medicine production, or as a solvent for such things as cleaning septic tanks (63,87 91). The remaining 5% is used as a chemical intermediate or solvent in the production of pesticides, waxes, gums, resins, tars, and chemicals such as chloroacetic acid (87.91). TCE has found some limited use as a surgical anesthetic and analgesic but is no longer

widely used for these purposes (15,76,87,97,103). Until recently, it was also a common constituent of many consumer products such as spot removers, rug cleaners, and air fresheners (51) but recent events which classed TCE as a hazardous substance prompted discontinuance of its use for these materials.

Properties of TCE

TCE is a colorless liquid with a sweetish odor that resembles chloroform. It is an unsaturated chlorinated hydrocarbon that is sparingly soluble in water but is readily miscible with organic solvents such as ether, chloroform, or alcohol (15,45,76,103). Its important physical properties are listed in Table 2 while nomenclature and other information are shown in Table 3. Since its oct and! water partition coefficient is 195 and therefore in the range of 100 to 1000, Roberts et al. (74) classify it as moderately hydrophobic. The United States Environmental Protection Agency (EPA) has designated it a "Hazardous Substance" (89) and has included it on the list of 129 priority pollutants (41,94).

Table 3. TCE Nomenclature and Identity Information.

Parameter	Value
Chemical Name	ethene, trichloro-
Common Names	ethylene, trichloro- acetylene trichloride ethinyl trichloride trichloroethylene TCE Trilene Trike
CAS Registry Number	79-01-6
Empirical Formula	C ₂ HCl ₃
Structural Formula	c_1 c_2 c_4
Molecular Weight	131.40
Percentage Composition:	
Carbon: Hydrogen: Chlorine:	0.77%

Note: Data for this table summarized from references 15, 45, 76, 87, 97, and 103.

Health Aspects of TCE

Any effect of TCE upon man is generally due to exposure through inhalation, skin absorption, and/or ingestion (15,43,76,87). Each of these routes of exposure present distinct problems separately and in combination.

Inhalation is the route of exposure most widely studied and cited in the literature because TCE is used so extensively in industry (87,97). The most predominant physiological effect due to inhaling TCE is depression of the central nervous system (CNS). This effect is the limiting factor used to determine Threshold Limit Values for industrial airborne exposures (15,43). CNS depression, along with loss of visual acuity, loss of coordination, mental confusion and fatigue, is of particular concern with acute exposures. For instance, in a two hour exposure of a volunteer to an airborne concentration of 1,000 parts per million (ppm) TCE, Vernon and Ferguson (93) found adverse effects on the subject's motor skills and visual percaption. The same effects were absent after similar exposures at concentrations of 300 and 100 ppm (93). This parallels studies of industrial exposures in which reported effects are generally associated with high transient concentrations instead of time weighted average values during a particular shift (43).

Liver and kidney damage in man has not been definitely linked to TCE exposure in industrial settings (43 87,97,

103). However, liver failure, following use of TCE as an anesthetic, has been observed in patients with complications such as malnutrition, toxemias, and burns (88). Additionally, liver damage in laboratory rats was demonstrated in studies of the synergistic effects of TCE and drugs (5,13).

Absorption of TCE through intact skin is possible but is not significant enough to cause systemic injury. It can, however, defat the skin and cause topical dermititis (15,43,97).

Little information was found concerning the toxicity and distribution of TCE due to oral ingestion. TCE is reported to be readily absorbed from the gastrointestinal tract since it is a small, uncharged, lipophilic molecule (47,61). The acute oral LD50 of TCE in rats is reported as 4,920 mg/kg (60). Acute poisoning of humans due to ingestion of TCE has produced symptoms of gastrointestinal upset, narcosis, and occasional cardiac abnormalities. Reports indicate these symptoms have been produced in adults who ingested 15-25 milliliters (ml) of TCE. Similar symptoms were produced in a child who ingested only 5 ml (61). The reviewed literature contained no reference to the effects of chronic ingestion of low levels of TCE.

TCE was classified as a possible carcinogenic agent as a result of a National Cancer Institute (NCI) study that

indicated oral ingestion of TCE can result in hepatocellular carcinomas in mice. In the NCI study, male and female rats and mice were intubated daily for 18 months with TCE dissolved in corn oil. Average daily TCE doses given were: male and female rats, 549 and 1,097 milligrams/kilogram body weight (mg/kg); male mice, 1,169 and 2,339 mg/kg; female mice, 869 and 1,739 mg/kg. While none of the rats developed hepatocellular carcinomas, 30.6% of the mice given the low dose and 43.2% of the mice given the high dose developed hepatocellular carcinomas (43,60,61).

The NCI study was criticized immediately upon publication because of the single daily administration of very large quantities of TCE. With such quantities, the distribution, metabolism, and elimination of TCE could have differed significantly from that at lower doses (61). Another criticism pointed out that TCE used in the bioassays contained epichlorohydrin and epoxibutane as stabilizers at levels high enough to possibly suggest they could have accounted for the carcinogenecity in the study. Regardless of criticism, the results of the study have generally been accepted because the grade of TCE used was representative of TCE used industrially (60,88).

Despite the NCI study, there is apparently no evidence that definitely links TCE to cancer in man (43). Furthermore, TCE has not been found to exhibit teratogenic or mutagenic properties in studies with lab animals by

either oral or inhalation routes of exposure (48,61,88, 97).

TCE Occurrence in Groundwater

Since TCE does not occur naturally in the environment (51,63), its existence in groundwater must be considered anthropogenic pollution (74). Indeed, the wide use of TCE offers such tremendous potential for pollution, it has been described as being "ubiquitous" in the environment (51,94). However, as shown by Table 4, other synthetic organic chemicals besides TCE are found in groundwater. In most cases, contaminated groundwater contains more than one of these chemicals with one or two of the compounds present at relatively high concentrations and one or more other compounds present at lower concentrations (20).

Generally, industrial discharges such as accidental spills, leaking storage tanks, illicit dumping, and improper disposal at dump sites have been cited as major sources of contamination (51,63). Specifically, the EPA listed the Findley, Minnesota waste dump as the most hazardous of 418 waste sites targeted for cleanup. One of their major violations had resulted in significant TCE contamination of the local aquifer (59). In the first criminal charges filed under the Resource Conservation and Recovery Act (RCRA), a federal grand jury indicted a leather tannery in Massachusetts for illegal disposal and

Table 4. Synthetic Organic Chemicals Most Commonly Found in Groundwater (92).

Trichloroethylene	Benzene
Tetrachloroethylene	Chlorobenzene
Carbon Tetrachloride	Dichlorobenzenes
l,l,l-Trichloroethane	Trichlorobenzenes
1,2-Dichloroethane	l,l-dichloroethylene
Vinyl Chloride	cis-1,2-dichloroethylene
Methylene Chloride	trans-1,2-dichloroethylene

Table 5. Occurrence of TCE in Drinking Water (92).

Survey	No. Samples	No. Positive	Range of TCE, ug/l
State Data	2,894	810	Trace - 35,000 .
NOMS	113	28	0.2 - 49
NSP	142	36	Trace - 53
CWSS	452	15	0.5 - 210

Note: State Data - from various state reports on local contamination problems in response to contamination incidents.

NOMS - National Organics Monitoring Survey

NSP - National Screening Program

CWSS - Community Water Supply Systems

storage of TCE (49). In another case, improper use of TCE to remove grease from a septic tank contaminated seven private wells in Long Island, New York (35,51). In Los Angeles County, California, 31 municipal wells in the San Gabriel Valley were closed because of high levels of TCE (20). In Bucks and Montgomery counties of Pennsylvania, 15 communities or towns also closed wells beause of TCE contamination (20,63).

TCE contamination is not limited to these examples. Of the 14 chemicals listed in Table 4, TCE has been the one detected most frequently in groundwater samples (20,92). The extent and magnitude of TCE contamination is illustrated by data from the EPA shown in Table 5. The table shows contamination levels as high as 35,000 micrograms/liter (ug/1) but most levels reported were less than 10 ug/1. The state data show higher levels of contamination because these samples were analyzed in response to particular incidents such as spills, monitoring of hazardous waste sites, or citizen complaints of taste and odor problems (92).

Since TCE may be present in groundwater used as a drinking water source, the question arises as to what is a safe level to prevent health risks to humans? As yet, this question has not been fully answered, but various levels have been recommended. In 1978, as recommended by the EPA Criteria and Standards Division, the suggested no adverse

response level (SNARL) was 4.5 ug/l (63). In 1980, the National Academy of Science Safe Drinking Water Committee (NAS) recommended a SNARL of 15 mg/l which did not account for TCE's potential as a carcinogen (61). This potential was taken into account in later calculations by both the NAS and the EPA's Cancer Assessment Group (CAG) to calculate concentrations which, if consumed over a lifetime (70 years) at two liters per day, might result in excess lifetime cancer risks of 10-4 (1:10,000), 10-5 (1:100,000), and 10-6 (1:1,000,000) (92). These concentrations are shown in Table 6. The two groups calculated different concentrations for the cancer risks but all values were within the EPA's probable recommended Minimum Contaminant Level of 5-500 ug/l (92).

Soil Environment

The total soil environment is made up of solid, liquid, and gaseous phases which contain their own physical, chemical, and biological environments. Within these phases are gas:liquid, liquid:solid, and solid:gas interfaces which contribute to the complexity of the soil.

The solid phase is made up of minerals, amorphous precipitates, and organic particles that vary extensively in composition, particle size distribution, and particle surface area depending upon the soil type and depth (1,2). The variation of a soil with depth in its horizontal layers or horizons is one way to classify a particular soil.

Table 6. Projected Cancer Risks for Drinking Water Concentrations of TCE (92).

Projected Cancer	TCE Concentration	in Water, ug/l
Risk	CAG	NAS
10-4	280	450
10-5	28	45
10-6	2.8	4.5

Table 7. Variation in Concentration of Microorganisms with Depth for a Typical Mineral Soil (1).

Depth,	Organisms/gram of soil (thousands)				
cm	Aerobic Bacteria	Anaerobic Bacteria	Actinomycetes	Fungi	Algae
3-8	7,800	1,950	2,080	119	25
20-25	1,800	379	245	50	5
35-40	472	98	49	14	0.5
65-75	10	1	5	6	0.1
135-145	1	0.4	-	3	-

Basically, soils consist of a profile with three layers, the A, B, and C horizons. The surface soil, or A horizon, contains the roots of plants, small animals, and the highest density of microorganisms since it also contains the highest concentration of organic material. Below this is the B horizon, which has less organic matter, roots, and microorganisms. The C horizon, which underlies the B horizon, has very little organic material and a low concentration of microorganisms (1,7).

The organic matter of soil has resulted from the decomposition of plant and animal remains that come in contact with the soil. As the soil microorganisms decompose a residue, the original material is converted to organic complexes which contain, among other things, aromatic and unsaturated ring structures carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, methoxyl, and amino groups (2). As reported by Felsot and Dahm (23), because of these functional groups, organic matter contributes 25-90% of the Cation Exchange Capacity (CEC) of many soils.

Black (7) defines the CEC as the sum of the exchangeable cations of a soil. It indicates the measure of the cations held by the clay and organic matter of soil which can be reversibly replaced by cations of acid and salt solutions. The CEC is usually expressed in terms of milliequivalents of ions exchangeable per 100 grams of soil. The soil particles themselves consist of aggregates of individual particles of silt, sand, and clay. These particles are classified according to size by the following scheme: clay, 0-2 um; silt, 2-50 um; sand, 0.050-2 mm (11). These particles usually occupy only 40-80% of the soil volume. The rest of the space is composed of pores filled with air and water.

The amount of pore space within a soil depends upon the texture, structure, and organic matter of the soil. Clays generally have a high percentage of pore space with very small pores while sandy soils have large pores but less pore space. Soils high in organic matter also have small pores, or micropores, which contribute to their ability to retain water (28). One aspect of micropores is that the water retained within them may be considered immobile compared to the mobile water which flows through larger pores. The pore space occupied by immobile water has been called the immobile domain with the rest of the pore space classified as the mobile domain (74). Consistent with this nomenclature is that of Houle and Long (33) who report that the effective pore space or porosity of most soils is only 90% of the total volume of pore space within the soil.

The water phase within the soil contains two components. One is the free or gravitational water that freely flows through the pores due to gravity. The other component is water which is held by the soil due to capillary

action because of the polar nature of water molecules and hydrogen bonding with polar surfaces of the soil. This water is held with a tension of about 1/3 atmosphere and will not freely drain from the soil (2). When the water content of a soil is due to that held by capillary action, the pores also contain large amounts of air and the soil is considered unsaturated. When the pore space is completely filled with water, practically no air or gas phase is present and the soil is saturated (11).

It is clear, then, that the gas and liquid phases of the soil are interrelated. As water moves into the pores, the gas is displaced; the converse is also true. The gas phase within the soil is not exactly the same as that of the atmosphere because of oxygen consumption and carbon dioxide production by microorganisms and plant roots. carbon dioxide content of soil air usually ranges from 0.3 to 3.0% compared to 0.03% for the atmosphere (2). The oxygen content in soil air is normally below 21% with a drop proportional to the carbon dioxide increase. Since a concentration gradient exists between the atmosphere and the soil air, it is understandable that the surface soil has an oxygen concentration similar to the atmosphere while the lower horizons show lower oxygen contents. Also, the carbon dioxide levels in soil air generally increase with increasing horizon depth (2,28). Saturated soils, however, can quickly become anaerobic because the oxygen demand by

soil microorganisms can deplete the dissolved oxygen within a few hours (1,2).

Alexander (1) lists the five major groups of soil microorganisms as bacteria, actinomycetes, fungi, algae, and protozoa. Bacteria are the most prominent group because they usually outnumber the other four groups combined. Bacteria are usually attached to the soil particles through electrostatic attractions or due to their extracellular secretions. The number of organisms that move with the soil water is very limited since they usually remain attached to the soil particles.

The concentration of bacteria and other microorganisms can vary widely depending upon the type, moisture content, and organic composition of the soil. Concentration of microorganisms generally parallels the concentration of organic matter in soil as discussed earlier. Table 7 shows the variation in concentration of microorganisms with depth of a mineral soil as reported by Alexander (1). Additionally, Alrichs (2) states that nearly all microorganisms are found in the A horizon and that organic molecules that reach the lower horizons stand a greatly reduced chance of biodegradation.

Other factors affect the population of microorganisms and their proliferation. The optimum moisture level for growth of many aerobic soil bacteria is reported as 50-75% of the moisture holding capacity of soil. Fluctuations in

this moisture level can cause fluctuations in the numbers of microorganisms (1,27). Another factor is addressed by Alrichs(2) who states that the microorganisms usually exist in a substrate limited growth until incorporation of additional organic matter stimulates activity and growth. neutral pH is considered optimum for most microorganisms (1,27), but many can exist at pH as low as 3.0 (1). perature affects the rate of growth; an increase in temperature stimulates biological activity up to a point, while a decrease in temperature can curtail activity. the key nutrient required to decompose organic matter. Ιf the soil is high in readily available nitrogen, microorganisms need no additional source. Conversely, substrates with low nitrogen content may require addition of ammonium or nitrate sources of nitrogen before biodegradation of organics can occur (1).

Chemical Transport in Soil

With an understanding of the toxicity of TCE and the nature of the soil environment, attention can be turned to the factors that govern the transport of TCE through soil. Abundant literature is available concerning experimental studies of the fate of organic chemicals in soil or sediment systems. The vast majority of these studies have dealt with pesticides while a number of others are concerned with trace level organics in aquifers. While TCE has not been one of the chemicals widely studied, concepts

and principles from studies with other chemicals apply and can yield valuable information.

When a chemical is introduced into the soil environment, the four processes that basically affect how that chemical is transported through the soil are volatilization, dispersion, sorption, and degradation (10,28,74,77). Each of these processes will be discussed with particular emphasis on adsorption and degradation.

Volatilization

Trichloroethylene, as evidenced by its Henry's Law constant, is volatile. In surface waters, volatilization is considered the most significant fate of TCE (52,94). Dilling et al. (19) found the evaporative half-life of a 1.0 mg/l aqueous solution of TCE to be 21 minutes when stirred, but approximately 90 minutes when only intermittently stirred. Jensen and Rosenburg (34) found that a TCE concentration of 1.0 mg/l had an evaporative half-life of 3.44 days in a partly open 20-liter tank under quiescent conditions.

Little data is available on volatilization rates of TCE or other chemicals from soil. Two studies which briefly addressed this are those of Bouwer et al. (10) and Tomson et al. (83), both of which involved trace organic behavior in rapid infiltration sites. Neither of these studies, however, quantitatively accounted for volatilization losses. Bouwer et al. (10) reported that

volatilization appeared to be the most important mechanism for chloroform removal in soil columns flooded with municipal wastewater that had been biologically treated. To a lesser degree, tetrachloroethylene and 1,1,1trichloroethane were lost as a result of volatilization. similar studies, Tomson et al. (83) estimated volatilization losses for a number of volatile organics, including TCE. Their estimates were based upon factors from conditions dissimilar to their own studies and showed greater than 99% volatilization losses for some of the compounds. However, as they pointed out, their estimates showed much greater losses than were accounted for by mass on the influent and effluent streams and balances illustrated the difficulty in predicting volatilization losses.

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Dispersion

Flow through a porous medium can cause a chemical in solution to disperse or spread due to varied permeability of the medium, fluid mixing through pores, and molecular diffusion (30,74,77). Soil contains tortuous pore structures that provide varied path lengths for fluid movement which allows for a degree of mixing. This effect has been termed hydrodynamic dispersion. Additionally, the diffusion of a chemical into stagnant pores or immobile domains will also spread the movement of a chemical by slow

release from the pores when the chemical or concentration front has passed (30).

Dispersion is accounted for in the following transport equation that describes one dimensional flow in a saturated, unconsolidated, homogeneous medium (6,24):

$$-u \frac{\partial c}{\partial x} + D \frac{\partial^{2} c}{\partial x^{2}} - \frac{\rho_{b}}{e} \frac{\partial s}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_{m} = \frac{\partial c}{\partial t}$$
(1)

where D = dispersion coefficient

C = solute concentration in aqueous phase

u = average fluid velocity

x = distance in direction of flow

e = soil porosity

 $\rho_{\rm b}$ = soil bulk density

S = mass of solute adsorbed per unit dry mass

t = time

rn = reaction term

In use of this equation, Roberts et al. (74) state that the value of D determined by laboratory studies or theory was not a good predictor of D for natural aquifers due to the wide spatial variations in the permeability of aquifiers. For aquifers or large field studies, dispersion should be accounted for by tracer studies (24,74).

In their study of some nonpolar organic compounds (chlorinated benzenes, toluene, and tetrachloroethylene), Schwarzenbach and Westall (77) did not attempt to quantitatively account for dispersion. In solving the

transport equation for different theoretical adsorption they considered dispersion rate constants, be insignificant. In studies of movement of the chlorobenthrough columns packed with fine sand, they graphically compared experimentally determined elution curves with computed elution curves using various known dispersion coefficients. The experimental curves were similar to computed curves for values of dispersion coefficients larger than what they expected particle size distribution and fluid velocity used. attributed the added dispersion to that due to experimental apparatus and sampling technique.

Adsorption

Definition and Description. Adsorption, according to Weber (99), is a surface phenomenon that involves the concentration of a substance at an interface between two phases. While these interfaces can be liquid:liquid, gas:liquid, or gas:solid, the one of interest in this study was the liquid:solid interface. The two main driving forces in adsorption are:

- 1. The solvophobic (or hydrophobic, in aqueous systems) nature of the solute within the solvent.
- 2. The degree of affinity of a solute (or adsorbate) for the solid surface (or adsorbent).

Adsorption is commonly classified into three different types: exchange, chemical, and physical.

Exchange adsorption is a result of electrical attraction of an adsorbate for an adsorbent which allows ions in solution to bind with charged sites on the solid surface (28,99). Chemical adsorption (or chemisorption) also involves specific site bonding, but instead of ionic bonding, a chemical bond is formed between the adsorbate and adsorbent which prevents free movement of the molecule on the surface. Chemisorption is also characterized by a high heat of adsorption (30-80 kcal/mole) (28,99). allows adsorbent site saturation low at adsorbate concentration and adsorption at elevated temperatures where physical adsorption is not of much consequence (28). physical adsorption, the heat of adsorption is generally low (2-10 kcal/mole) and the adsorbed molecule is not fixed to a specific site but can freely move around the surface. This adsorption is largely due to Van der Waal's (or intermolecular) forces which attract nonionic, nonpolar molecules such as hydrocarbons in water (8,99). intermolecular forces that act in adsorption are direct and induced ion-dipole and dipole-dipole interactions and transient dipole-induced dipole interactions termed Van der Waal's--London Interactions. Adsorptive forces include hydrogen bonding and hydrophobic interactions between the solute and adsorbate (28).

While distinctions are made between the different types of adsorption, it is commonly agreed that adsorption

of an organic molecule can rarely be attributed to only one type. Rather, it is felt that adsorption can be a combination of any or all of the different types, particularly a combination of physical and chemical adsorption which are not always easily differentiated (8,28,99). This is particularly true in soils, which are composed of heterogeneous substances (28).

When an adsorption system is in equilibrium, a Isotherms. definite distribution of solute exits between the liquid and solid phases. This distribution is described by an isotherm which relates the mass of solute adsorbed (adsorbate) per unit mass of adsorbent to the equilibrium concentration of solute in the liquid phase. To establish data to describe an isotherm, a known amount of adsorbent is added to a known amount (or concentration) of solute (or adsorbate) in solution. The system is allowed to reach equilibrium with the amount of adsorbate removed from solution in the liquid phase considered to be adsorbed. This data can be used in a number of different equations to generate isotherms such as the Langmuir, Freundlich, or linear (28,99).

The Langmuir equation was developed from a kinetic and thermodynamic conceptual basis for the adsorption of gases onto solids. The assumptions used in its development were:

(1) constant energy of adsorption which is independent of surface coverage; (2) adsorption is localized with no

interaction between adsorbate molecules; and (3) maximum adsorption consists of a saturated monolayer of solute molecules (8,28,99). The equation can be written as:

$$X/M = \frac{Q \circ bC}{1+bC}$$
 (2)

Where X/M = mass of solute adsorbed per unit mass of adsorbent

Q° = mass of adsorbed solute per unit mass of adsorbent required to form a complete monolayer on the surface

b = a constant indicative of the energy of adsorption

C = equilibrium concentration of solute in solvent

An equation related to the Langmuir isotherm is the Emmet, and Taylor (BET) isotherm. Ιt Brunauer, is conceptually similar to the Langmuir except the BET assumes multilayer adsorption on the surface sites (99). is rarely used to describe adsorption and will not discussed further In fact, the Langmuir equation is very seldom used in soil adsorption systems because the heterogeneity of the soil surfaces quite invalidates the assumption of constant energy of adsorption (28). Of the literature reviewed for this research, no use of the Langmuir isotherm was found.

An often used equation in soil adsorption studies is the Freundlich isotherm, an empirical equation stated as:

$$X/M = K_F C^{1/n}$$
 (3)

Where X/M = mass of solute adsorbed per unit mass of adsorbent

C = equilibrium concentration of solute

K_F = an equilibrium constant indicative of adsorptive capacity

1/n = a constant indicative of adsorption
 intensity

This equation has a major disadvantage in that it places no limit on the amount of adsorption that can occur on a surface as equilibrium concentration increases. Theoretically, it can predict that adsorption will infinitely, however, it should not be extrapolated past the range of solute concentrations over which it is developed (8,99).The Freundlich equation agrees reasonably well with the Langmuir equation over moderate concentrations of C but not well at high concentrations. It does not reduce to a linear equation at low concentrations as does the Langmuir (99). Nevertheless, it has been widely used in soil adsorption studies with a variety of compounds such benzene (75); 2,4-D amine as: and atrazine (66); hexachlorocyclohexane (95); 2,4,5-T (47); organophosphorous and carbamate insecticides (23); DDT, dieldrin, lindane, diazinon, and parathion (79); and TCE (70). majority of these studies, the value of the constant 1/n is very close to unity.

Another equation often used is a form of the Freundlich equation with 1/n equal to one. In this case, the equation describes a distribution or partitioning

between the two phases by a linear relationship (28,38). The equation for the linear isotherm is:

$$X/M = K_pC (4)$$

Where X/M = mass of solute adsorbed per unit mass of adsorbent

C = equilibrium concentration of solute

 K_D = linear partition coefficient

This isotherm equation has found wide use in many soil adsorption studies, particularly at low solute concentrations. Included among the compounds to which this isotherm has been applied are: polynuclear aromatic hydrocarbons (PAHs) (55,56); toluene, tetrachloroethylene, and chlorinated and methylated benzenes (77); pyrene, methoxychlor, naphthalene, and benzene (38); and various polychlorinated biphenyls (PCBs) (50).

Related to the linear partition coefficient or constant, K_p , is a coefficient, K_{OC} , based upon the fraction of organic carbon present in the adsorbent (28,30,38,39,55). The relationship is:

$$K_{OC} = \frac{K_{D}}{f_{OC}}$$
 (5)

Where f_{OC} = fraction of organic carbon in the adsorbent

Similarly, in several studies (23,65,75) the Freundlich equilibrium constant, KF, was normalized on the basis of organic carbon as:

$$K_{OCF} = \frac{K_F}{f_{OC}}$$
 (6)

Organic Carbon. The use of the coefficients of Equations 5 and 6 emphasizes the importance of organic carbon content in adsorption. These coefficients allow comparison of adsorption of neutral molecules based solely upon organic carbon content without regard for adsorption due to other properties of the soil. Thus, for a series of soils tested with the same compound (assuming no other property affects adsorption), the K_{OC} or K_{OCF} for each of the soils should not vary significantly from the average for all of the soils (28,30,38). Laboratory studies have illustrated the relation between adsorption and organic carbon content.

Means et al. (55) studied the adsorption of four PAHs on 14 different soils and sediments which had organic carbon contents of 0.11 to 2.38%. They found a significant correlation between the K_p for each PAH and the organic carbon content of each soil. The soils with the higher organic carbon content exhibited higher K_p 's which, when converted to K_{OC} 's, converged on the mean value for all the adsorbents studied. The average K_{OC} 's were then used to compare the strength of adsorption of the different PAHs.

Schwarzenbach and Westall (77) also reported a highly significant correlation between K_p and organic carbon content but only when the adsorbents contained more than 0.1% organic carbon. Their study, conducted with a series of chlorinated benzenes and natural aquifer materials,

found little correlation for K_p when the organic carbon content was less than 0.1%.

Sharom et al. (79) compared the adsorption of aqueous insecticide solutions on four different soils with organic carbon contents of 0.7, 2.5, 2.8, and 75.3%. The insecticides included six organophosphorus, four organochlorine, and two carbamate insecticides of different chemical structures and water solubilities that ranged from 0.0012 mg/l to a totally miscible compound. The $K_{\mathbf{F}}$ vlaues obtained from batch isotherm tests for each of the 12 solutions decreased for each of the soils in the order of decreasing organic carbon content. This relationship was also reported by Richter (70) in a study of TCE in aqueous solutions at concentrations up to 1.1 mg/l with peat and a variety of inorganic soils.

Felsot and Dahm (23) approached the organic carbon: adsorption relationship in a different way. They initially determined adsorption isotherms for some organophosphorus and carbamate insecticides with various soils, then oxidized the organic matter of the soils with hydrogen peroxide. Redetermination of adsorption isotherms with the oxidized soils showed that adsorption decreased within the same soils in proportion to the fraction of organic carbon destroyed.

Octanol: Water Partition Coefficient. According to Karickhoff (39), the organic carbon in soil acts in the

same manner as a solvent in a water:immiscible solvent extraction. Based upon this concept, he proposed a correlation between the linear partition coefficient (K_p) and a solvent:water partition coefficient. He developed this correlation for a series of polycyclic aromatic compounds and chlorinated hydrocarbons that had water solubilities ranging from 1 microgram/liter (μ g/1) to 1,000 milligrams/liter (μ g/1) (38). He correlated the octanol: water partition coefficient (μ g/1) of the individual compounds with μ g/2's determined for the individual compounds and averaged for three different sediments used as adsorbents. Linear least squares fitting of the data resulted in the following relationship:

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$$K_{OC} = 0.63 K_{OW} \tag{7}$$

From Equation 5,

$$K_{p} = 0.63 K_{ow} f_{oc}$$
 (8)

A similar relationship was developed by Schwarzenbach and Westall (77) as:

$$log K_p = 0.72 log K_{ow} + log f_{oc} + 0.49$$
 (9)

These equations are useful to predict K_p within a factor of two for nonpolar organics and soil or sediment but are truly valid only for the compounds and range of concentrations used in the studies. Extrapolation beyond this may increase the error of the estimate (38,77).

Other Factors. Of the literature reviewed, only Felsot and Dahm (23) reported a high correlation between adsorption

and CEC of adsorbate. Since they found an even higher correlation between the organic carbon content and CEC, they concluded the correlation between adsorption and CEC was related more to the organic content of the CEC than to the CEC itself. Others (40,50,55,75) reported the CEC of soil adsorbents but made no correlation between adsorption and CEC. In these studies (40,50,55,75) the soils with higher organic carbon content generally had higher CECs except for some soils with significant clay contents.

The pH of a soil system can affect adsorption for weak acid and weak base organics. These compounds can exist in either an ionized or non-ionized form depending upon pH. At low pH, weak acids are in the free acid state while weak bases are cationic; both compounds are adsorbed more highly in these forms than at higher pH (28,47). Generally, though, adsorption of nonpolar compounds shows no marked pH effect unless the pH of the soil solution was changed drastically enough to produce a change in soil components which affected adsorption (27). There is little discussion on pH effects in the literature. Felsot and Dahm (23) found no correlation between adsorption and soil pH. Other studies (40,47,50,55,56,65,75,95) list soil pH values but do not discuss them in any way.

One aspect of pH effects is that pH, organic matter, CEC, and other soil properties are so interrelated it can be difficult to separate the effect of pH alone (28).

Additionally, soil pH measurements are determined on slurries of 1:1 or 1:2 soil:water ratios (7,64) which might not accurately define the hydrogen ion activity of the soil.

Surface Effects. Since adsorption is a surface phenomenon, the extent of adsorption should be proportional to the surface area of the adsorbent (99) which, in the case of soil adsorbents, is related to the particle size (38,77). Surprisingly, few references to the effect of particle size were found. In addition, there was no general agreement on the particle size to be used for batch isotherm tests as illustrated by Table 8 which presents data from some representative studies.

Karickhoff et al. (38) were concerned not with increase in surface area with the decrease in particle size, but with the difference in organic carbon content with different particle size fractions. They reported the organic content of soils is most heavily found in the fines fraction (less than 50 microns). They reported that adsorption by smaller particles is basically due to the organic carbon content, not increased surface area. However, when correcting for organic carbon content by use of Koc, they found, for the same organic compound, the Koc of the sand fraction to be less than 50% of the Koc for the fines fraction. This indicated a certain dependence upon particle size. For nonporous adsorbents, such as sand

particles, surface area available for adsorption is inversely related to particle diameter (99).

Schwarzenbach and Westall (77) approached this factor in a different manner. Their concern was that washing soil samples prior to use in adsorption studies can affect the results of the study. They found that increased length of washing lowered the K_p of a sand for a series of chlorobenzenes. The lowered K_p resulted from removal of clay and silt particles which were attached to the sand particles but could be removed through continued agitation and washing. They concluded that to obtain representative sorption data of a particular sample, soil should not be washed before use.

As shown by Table 8, various particle sizes have been used to develop isotherms. These studies, though, provide no duplication of compound with different particle sizes to see if a difference in adsorptive capacity exists due to particle size. A difference may not be expected for nonporous adsorbents. For highly porous organic fractions, however, breaking large particles into smaller particles might open sealed interior pores and surface areas normally not available for adsorption. Such an increase in surface area could increase adsorptive capacity which would indicate a dependence of adsorptive capacity on particle size (99).

Table 8. Particle Size Information From Representative Soil Adsorption Studies.

Particle Size, mm	Particle Size Effect Discussed	Type of Study	Reference
< 0.833	No	(1)	56
< 0.075	No	(1)	70
< 4	No	(2)	40
< 0.833	No	(1)	55
Not listed	No	(1)	75
(3)	Yes	(1)	38
< 0.150	No	(1)	95
Not listed	No	(1)	47
(4)	Yes	(1)	50
< 2	No	(1)	65
< 2.3	No	(1)	23
< 0.125	Yes	(1)	77
0.63-0.125	Yes	(1)	77

Notes: 1. Batch isotherm studies.

- 2. Packed column elution study.
- 3. Separated into silt, sand, clay fractions.
- 4. Results discussed on basis of surface area measurements.

Adsorption Equilibrium. Three steps are involved in the overall adsorption process (99):

- 1. Transport of the adsorbate through the bulk of the solution to the surface of the adsorbent (film diffusion).
- 2. Diffusion into the pores of the adsorbent (pore diffusion).
- 3. Adsorption at the surface.

For nonporous adsorbents, step 2 is fairly insignificant (28). Since the adsorption step itself is quite rapid, the rate limiting step in soil:water adsorption systems is usually either step 1 or 2 (23,99).

If one assumes similarity with carbon adsorption, the rate limiting step depends upon the degree of contact the particle has with the aqueous solution. In batch isotherm tests, the system is continuously shaken so the degree of agitation is high. In this case, step 2 or 3 would be the rate limiting step. In column studies, a laminar boundary layer may surround the soil particle and step 1 can control (98).

In batch isotherm studies, equilibration times vary depending upon the compound, concentration, and adsorbent. Some investigators do not determine an equilibration time but use a standard 24 or 48 hour contact time. Table 9 lists some equilibration times from isotherm studies. Compared to batch studies, the number of soil column

Table 9. Reported Equilibration Times for Batch Isotherm Studies.

Compounds(s)		ntration s, ug/l	Equilibration Time, Hours	Reference
TCE	11 -	1,100	18	70
Chlorobenzenes	20 -	100	18	77
PAHs	0.02 -	100	20	55
Benzene	3 -	1,000	16	75
2,4,5-T	510 -	45,000	24	47
Organophosphorus and carbamate insecticides	40 -	400	2	23

studies reported is small. Some parameters of applicable packed column tests are listed in Table 10.

A concept of interest in soil column studies is local equilibrium. This condition is achieved when the rate of mass transfer of a solute to an adsorption site is fast compared to the pore velocity of water through the soil (34,40). In effect, this concept could indicate that flow rate affects adsorption.

study of chlorobenzene (CB), Flow rate. One dichlorobenzene (DCB), 1,2,3- and and trichlorobenzenes (TCBs) reported the effect flow rate had upon these compounds in a packed column of fine sand. feed to the column was with a constant concentration, C_{O} , of the compound at actual flow velocities of 8.7 \times 10⁻⁴ cm/sec (low) and 1.0×10^{-2} cm/sec (high). They reported effluent volumes in terms of pore volumes (PV) of water passed through the column with break-through considered when the concentration in the effluent (Ce) approximately equal to Co. Table 11 summarizes the results from this study. As shown in Table 11, the order of magnitude difference in flowrate had the most effect on TCB with less effect on DCB and virtually no effect on CB. number of PV until the compound appeared in the effluent until breakthrough, increased in the increasing Kow for both flow velocities. The earlier

Parameters From Packed Column Adsorption Studies. Table 10.

Size, cm Flowrate, length x i.d. cm/sec(l)	Flowrate, cm/sec(1)	Diff. noted with increased flowrate	Compound(s) Studied	Concentration, Reference ug/l	Reference
29x1.2	8.7x10-4 8.0x10-4 1.0x10-2	Yes	Chloro- benzenes	40	7.7
15x7.5	1.21x10-4	(2)	Pesticides	20-5,000	99
30.5x7.6	(3)	(2)	Pesticides	(4)	40
275×10	2.8×10-4 - 4.6×10-4	ON	Chloroform 1,1,1-tri- chloroethane tetrachloro- ethylene	1-10	10

Flowrate is pore water velocity. Not discussed. No flowrate given. Concentration not listed. £32£ Notes:

Table 11. Summary of Data from Packed Column Study (77).

Ch	und	
СВ	DCB	TCB
2.71	3,38	4.05
1.5	4	9
2.5	10	20
1.5	3	5
2.5	7	12
	CB 2.71 1.5 2.5	2.71 3.38 1.5 4 2.5 10

appearance of the compound and earlier breakthrough for high velocities may indicate lack of local equilibrium.

The fact that the compound did not appear in the effluent until after at least one PV indicated that adsorption can retard the movement of an advancing solute concentration front. In this case TCB was retarded the most. This illustrates the relationship between $K_{\rm p}$ and $K_{\rm ow}$ of Equation 8.

Retardation. Retardation of an advancing solute concentration front has been extensively discussed (65,66,72,74,77,83). If local equilibrium and linear adsorption are assumed,

$$\frac{dS}{dC} = K_p \tag{10}$$

With this relationship, the transport equation (Equation 1) can be used to predict retardation. If dispersion and reaction terms are neglected, Equation 1 becomes:

$$-u \frac{\partial C}{\partial x} = \left[1 + \rho_b K_p/e\right] \frac{\partial C}{\partial t}$$
Where
$$\left[1 + \rho_b K_p/e\right] = t_r$$
(11)

The term t_r is defined as the retardation factor which, within a soil column, would theoretically determine the number of pore volumes of water that would pass through before breakthrough. Since the values of b and e do not vary extensively within a given area, K_p determines the size of the retardation factor. Since K_p can be estimated

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according to Equations 8 and 9, the retardation term can also be estimated from knowledge of K_{OW} , f_{OC} , b, and e.

In a similar fashion, if a solute follows a Freundlich isotherm and local equilibrium exits, Equation 3 becomes:

$$X/M = S = K_F C^{1/n}$$
 (13)

$$\frac{dS}{dC} = K_F^{1/nC}^{1/n-1} \tag{14}$$

and the transport equation becomes:

$$-u \frac{\partial C}{\partial x} = \left[1 + \frac{\rho_b K_F 1/nC}{e}\right] \frac{\partial C}{\partial t}$$
 (15)

Where
$$\begin{bmatrix} 1 + \frac{\rho_h K_F 1/nC}{e} \end{bmatrix} = t_r$$
 (16)

The retardation terms of Equations 12 and 16 illustrate that with a solute that obeys a linear adsorption isotherm, retardation is independent of concentration. For a solute that follows a Freundlich isotherm, retardation is dependent upon concentration.

To this point, all discussion has centered upon adsorption of a solute from a solution. Very seldom, though, is an adsorbent challenged by a solution in which the solute maintains a constant concentration. Adsorption is a process of dynamic equilibrium. When the solute concentration in the contacting liquid decreases or is eliminated, there is a corresponding decrease in the adsorptive capacity (X/M) of the adsorbate. This proces is desorption.

Desorption. Desorption is commonly studied by batch equilibration in a method similar to adsorption isotherm A portion of soil is equilibrated with a known amount of solute. After equilibrium is established, all or a portion of the solution is removed and replaced with water containing no solute, thus lowering the equilibrium concentration. The container is then re-equilibrated and X/M values are calculated from the resulting equilibrium Any increase in concentration is assumed concentration. due to the mass of solute desorbed from the adsorbent (23,65.66,75,95). This procedure can be repeated as often as necessary to develop a desorption isotherm; however, other experimental losses such as volatilization, degradation, or precipitation must be accounted for so they do not unknowingly lead to an overcalculation of the amount of solute still adsorbed (66,75).

Desorption studies can produce isotherms which do not overlap adsorption isotherms. This noncoincidence of isotherms is known as hysteresis. The usual effect of hysteresis is that desorption isotherms show higher adsorptive capacity at lower equilibrium concentrations when compared to adsorption (23,28,47,77). Apart from unknown experimental losses, hysteresis can be due to nonattainment of equilibrium or to changes in the strength of adsorption during desorption over time (28,47). These

two causes may be interrelated and difficult to separate due to the heterogeneity of soil adsorbents (28).

Organic carbon content is a strong factor in desorption. Felsot and Dahm (23) found evidence hysteresis in conventional adsorption-desorption studies of five different organophosphorus and carbamate insecticides on five soils with varied organic carbon contents. found desorption decreased for each of the insecticides as the organic content of the soils increased. evidence of this relationship came from additional studies on portions of the high organic soils which were oxidized to reduce the organic content. Oxidized portions showed greater desorption than unoxidized portions for all pesticides tested. Similar results were shown with three isomers of hexachlorocyclohexane (HCH) at adsorption equilibrium concentrations of 20-100 ug/l (95). adsorption equilibration, each sample was subjected to at least four successive desorptions. The authors found the extent of hysteresis to vary among the different isomers but was consistently greater (less desorption) for the higher organic carbon soils. Neither of these studies, however, accounted for losses due to degradation, nonequilibrium, or volatilization.

One study which did account for such loss is that of Koskinen et al. (47) who characterized hysteresis of 2,4,5-T in desorption from soils at concentrations of

1.5-10 mg/l. They studied the effect of equilibration time on desorption by varying desorption times from 3-48 hours. Their initial studies found greater hysteresis (less desorption) for the longer desorption times which was counter to what was expected. After changing their experimental protocol to account for volatilization and biodegradation losses, actual hysteresis decreased for longer desorption times. This indicated that procedural methodology can significantly influence results.

Successive handling of desorption vials and repeated desorption steps with volatile compounds can introduce volatilization losses which, if not accounted for, can also influence apparent results. Rogers et al. (75) addressed this problem in their study of benzene in the 10-1,000 ug/l concentration range. During one phase of their adsorption-desorption studies their reaction flasks had an unrestricted headspace. In this case, a mass balance for adsorbed benzene, benzene in solution, and loss due to biodegradation accounted for only 1-12% of the mass of benzene applied. As they pointed out, volatilization was then responsible for loss of 88-99% of the benzene.

This type of loss by volatile compounds is the reason Schwarzenbach and Westall (77) did not attempt to determine desorption isotherms for the compounds listed in Table 11. They studied desorption by pumping a solution of the compound through a column until breakthrough occurred. At

this point the feed solution was changed to solute free distilled water which caused the adsorbed compounds to desorb from the soil columns. The combined breakthroughelution curves produced several points worth comment. From a mass balance on the solute in the effluents, they determined that all the material adsorbed on the columns subsequently desorbed. CLB exhibited breakthrough first, had the steepest breakthrough curve, and had a nearly symmetrical elution curve with very little tailing. DCB exhibited breakthrough second, had moderately sloped breakthrough and elution curves which showed moderate tailing. TCB showed breakthrough last and exhibited breakthrough and elution curves less steep than DCB but with extensive tailing. Viewed with Kow in mind, the slopes of the breakthrough and elution curves decreased and the amount of tailing of the elution curves decreased as the $K_{\mbox{\scriptsize OW}}$ of the compound increased. According to the authors, the tailing could have been due to the hysteretic nature of the adsorption-desorption process, adsorption-desorption kinetics, or the variation in strength of adsorption with different sites (nonequivalency of sites).

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In a similar column study, Rao et al. (65,66) determined breakthrough and elution curves for 2,4-D amine (50 and 5,000 mg/l) and atrazine (5 and 50 mg/l) in two soils. Both pesticides exhibited non-linear adsorption with Freundlich l/n values less than one. Consequently,

increased mobility of the pesticides was shown for the higher concentration with both soils. For instance, the 50 mg/l 2,4-D solution exhibited breakthrough at eight pore volumes for the high organic (3.87%) soil and three pore volumes with low organic (0.90%) soil. The 5,000 mg/l 2,4-D solution reached breakthrough at two pore volumes for the high organic soil and one pore volume for the low organic soil. Atrazine showed similar results. The shape of the curves was affected by solution concentration and soil organic content. High solute concentrations and low organic soil content produced steeper breakthrough and elution curves compared to low solute concentrations and high organic soil content. Trailing on the elution curve was much more evident in low concentrations and high organic content soils. The authors pointed out that the shape of the breakthrough and elution curves depended upon adsorption-desorption kinetics. Symmetrical breakthrough curves are normally obtained when local equilibrium exists while nonequilibrium normally produces asymmetrical curves (65). The trailing exhibited in this work was attributed to nonequilibrium.

Other described by Hamaker (30) as "one-shot leaching."

In this type of study a quantity of chemical is added to a soil column and its movement is traced as a function of water applied. One application of this method studied the

movement of synthetic pyrethroid insecticides in packed columns (40). The authors added a quantity of the chemical to the top of the column, then added one pore volume of water to the column and collected the effluent. No pesticides were detected in the effluent. Analysis of the different depths of the column showed very little penetration of the soil by the compounds. This indicated their immobility in soil. In a similar study, Sharom et al. (79) studied 12 insecticides with four different soils. They found all 12 insecticides were more strongly retained and resisted leaching with the higher organic soils compared to the lower organic soils.

Some possible differences between laboratory studies and actual field leaching were addressed by Hamaker (30). He reported that in chemical leaching in the field, intermittent rainfall can leach or desorb a chemical causing a downward migration of the chemcial. However, when the soil dries, capillary action can pull some of the water and chemical back towards the surface. Additionally, the tendency of tailing in one shot leaching is due to the same causes discussed earlier, i.e., difference between adsorption and desorption rates and nonequivalency of adsorption sites. One factor that differentiates one shot leaching from column studies with constant solute concentration is that one shot leaching begins with the compound intimately contacted with the soil. According to

Hamaker (28), this contact can cause higher adsorptive capacity and greater hysteresis than would occur with an equivalent amount of chemical in solution.

Degradation

Chemical Degradation

Studies inconclusive as to whether direct are photolysis is a means by which TCE is degraded. By using a closed system in which no volatilization could occur, Jensen and Rosenberg (34) detected significant no difference in TCE concentration for systems maintained in darkness compared to similar systems exposed to sunlight. Dilling et al. (19) studied the abiotic degradation of TCE exposed to sunlight in sealed ampules of 1.0 mg/l solutions with enough oxygen present to completely oxidize all TCE in In this case, sunlight the ampule. increased the reactivity of TCE to the point that its half-life was about 1.7 times shorter in sunlight than in darkness. The authors suggested the degradation products were dichloroacetic acid and hydrogen chloride from free radical oxidation. Any effect of sunlight on chemical reactions is minimal in soil because the radiant energy is strongly adsorbed by the soil. This reduces the chance photolytic reactions even at the soil surface (27) and basically eliminates them in the subsurface environment (74).

In their studies, Dilling et al. (19) did not differentiate between oxidation and hydrolysis; therefore, the experimentally determined first order reaction rate, 0.0065/month, is a combined rate due to both oxidation and hydrolysis. Hydrolysis alone, though, may not be a significant factor in degradation of TCE. According to work cited by Dilling et al. (19) TCE in water can resist hydrolysis at 100°C. The EPA reports that under normal conditions, TCE is not hydrolyzed in water (94). Reactions in an aqueous medium may be entirely different from those in a soil medium because soil has catalytic properties. Clays, organic and metallic ions, metal oxides, and various organic functional groups are possible catalysts for chemical reactions (27).

Biodegradation

Since the soil contains a living environment, any foreign substance added to it can be subjected to microbial degradation. Biological degradation of anthropogenic compounds by soil environments has been extensively studied. The overwhelming majority of work in this field has been dedicated to pesticides as illustrated by the extensive review presented by Goring et al. (27). Other compounds such as trichlorobenzene (54) and oil (67) have also been studied.

Any consideration of microbial degradation of organic chemicals added to the soil environment must be reviewed

with an understanding that many factors affect biodegradation. These factors, such as pH, moisture content, and oxygen level were previously discussed. Additionally, sometimes it is difficult to separate biodegradation from chemical degradation (27). One reason generally given for the resistance of anthropogenic compounds to biodegradation is that soil micoorganisms lack the enzymes necessary to transform the compound to a degree where it can be metabolized (1,27,46). Some resistant compounds include halogenated organics such as pesticides, trihalomethanes, and organic solvents such as TCE (46).

One biodegradability study of TCE was made by Taybak et al. (82) in their study of priority pollutants in static flask cultures. They tested 5.0 and 10.0 mg/l TCE concentrations in BOD dilution water that contained 5.0 mg/l yeast extract and was innoculated with settled domestic wastewater. After static incubation in the dark at 25°C for one week, a subculture was transferred to fresh medium. This medium was likewise incubated with additional subcultures at the end of the second and third weeks. Blanks accounted for volatilization and chemical degrada-At both test concentrations, TCE showed significant biodegradation after gradual adaptation. After blank corrections, the 5.0 mg/l concentration showed losses of 35%, 44%, 53%, and 50% for each of the succeeding weekly cultures. Likewise, the 10 mg/l concentration showed

losses of 16%, 34%, 54%, and 62%. Conditions of the test indicated these losses were due to biodegradation. Other studies, at much lower concentrations, have not shown such significant biodegradation.

Bouwer et al. (9) studied aerobic and anaerobic degradation of TCE in static flask cultures similar to Taybak et al. (82) with these exceptions: yeast extract was not added; concentrations ranged from 10-200 ug/1; aerobic cultures were incubated at 20°C; weekly subcultures were not used; anaerobic cultures were incubated at 35°C; and anaerobic cultures were seeded with anaerobically digested sludge. All cultures were compared to sterile blanks incubated to account for other losses. Aerobic conditions produced no significant degradation for the concentration range tested for any of the cultures during the 25 week incubation period. Anaerobic conditions showed a very slight degradation compared to sterile controls during the 16 week incubation; however, the authors felt the results were not conclusive.

A field study of groundwater recharge in California presented some evidence of biodegradation of various halogenated organics, including TCE. Roberts et al. (73) studied the decrease in concentration of various compounds in an observation well of an aquifer subjected to groundwater recharge by reclaimed water. When injection was halted, the adsorption capacity of the aquifer was

considered saturated because breakthrough of all compounds had occurred. TCE concentration then declined linearly from 10 ug/l to 2.5 ug/l at a rate of 0.003 ug/l/day when corrected for dilution. The authors considered this evidence of biodegradation. This rate found for TCE, however, was an order of magnitude less than that found for trihalomethanes, which degraded from 20 ug/l to 0.75 ug/l at a rate of 0.03 ug/l/day. The area under study was a silty sand and gravel aquifer 10 to 15 meters below the soil surface.

Wilson et al. (101) conducted a biodegradation study with samples of four different subsurface aquifer materials aseptically and uncontaminated with surface compounds studied 1,1 microorganisms. The were: dichloroethane; chloroform; 1,1,1-trichloroethane; trichloroethylene; tetrachloroethylene; toluene; benzene; and styrene. Solutions of these compounds at 1.0 mg/l were mixed with slurries of the subsurface materials and incubated in the dark for up 27 weeks. Periodically, samples were analyzed and compared to sterile controls. They found no evidence of biodegradation for 1,1-dichloroethane, chloroform, or 1,1,1-trichloroethane in any of the samples while toluene and styrene were slowly degraded in all four subsurface slurry systems. Chlorobenzene, tetrachloroethylene, and trichloroethylene showed detectable biodegradation in some but not all of the

subsurface samples. The reported rate for TCE was 1.3 to 2.3% of the initial compound per week.

The variation in biodegradation with variation in sample is not unusual. location The microbial population varies so considerably with location and depth that Goring et al. (27) consider this variation to be the most unpredictable factor involved in the degradation of pesticides and other chemicals in soils. Additionally, materials that are highly insoluble in water or are highly adsorbed by the soil can resist degradation in soil microcosms to a greater degree than would be shown in other media (27). With the large surface area provided by the material of the soil, the fine grained biodegradation by an attached film, or biofilm, proposed for organic substances in a porous medium such as soil (57,74). This film requires three separate but interrelated steps: mass transfer of the organic from the bulk of the solution to the attached film; biodegradation within the film; and film growth and decay. Since a detailed description of fixed film kinetics is not within the scope of this investigation, the reader is referred to McCarty et al. (57) and Rittman et al. (71) for further information.

Regardless of the manner in which biodegradation of TCE occurs, it appears the initial step is usually dehalogenation (46). Goldman (26) presented several

biological mechanisms for dehalogenation of halogenated short chain fatty acids. Dehalogenation is considered a necessary step before beta oxidation of the fatty acids can Neither Goldman (26) nor others, though, reported any particular scheme for dehalogenation of TCE. Kobayashi and Pittman (46) presented a general scheme for reductive dehalogenation by oxidation-reduction as shown in Figure 1. Essentially, this scheme depicts the transfer of electrons from reduced organic substances by microorganisms or abiotic mediators such as NAD, NADP, flavin, flavoproteins, hemoproteins, porphyrins, chlorophyll, cytochromes, glutathione. The mediators accept the electrons from reduced organic substances and transfer them halogenated compound. Free available electrons and direct contact between the donor, mediator, and acceptor of electrons are required for this scheme to function.

Parsons et al. (62) found evidence for this type of dechlorination of TCE in studies with several muck and mud samples. They found the initial chloride ion extracted preferentially formed cis-1,2-dichloroethylene over trans-1,2-dichloroethylene. This preference was attributed to the fact that water, as a polar solvent, prefers the more polar cis-isomer of dichloroethylene.

The literature contains many references to degradative pathways for numerous synthetic organic chemicals (27), including chlorinated aromatics (26,54). No reference,

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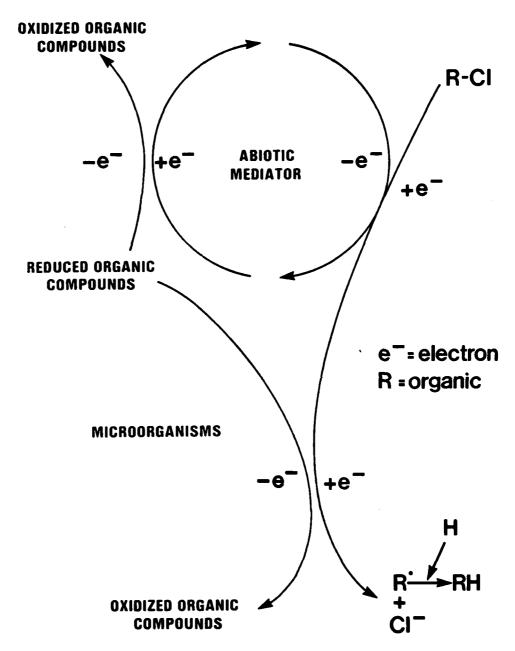


Figure 1. Possible Routes of Reductive Dechlorination (46).

however, was found to any mechanism or pathway for the degradation of TCE.

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Summary

The literature confirms that TCE is present in a significant number of groundwater sources. This is understandable since the production of TCE for 1981 (according to Table 1) was 365,000,000 pounds. If only 0.0001% of this were subsequently lost to groundwater, it could contaminate 8.76×10^{12} gallons of water at 500 ug/l. This volume is equivalent to the lifetime drinking water supply of over 640 million people.

Also widely documented is the correlation between adsorption and the organic content of soil. Little information exists, however, on the effects of flowrate on desorption. Furthermore, information on the adsorption, desorption, and movement of organic chemicals (except for pesticides) in soils at high concentrations is lacking. While some information is available on the movement of trace organics in aquifers (57,72,74), Richter's work (70) with low concentrations of TCE was the only soil adsorption study noted. Even Karickhoff's extensive review (39) of soil-organic chemical adsorption did not contain data for TCE although 13 other chlorinated hydrocarbons were listed. No studies were found which traced the movement of a spill or slug of TCE through soil. Additionally, degradation of

TCE has been studied, but under conditions dissimilar to actual field conditions.

Significant throughout the literature on column studies is the use of pore volume or void volume as a common descriptor for the amount of effluent collected from a column (28,30,33,40,65,66,77). This description is used to provide a common basis on which to correct for differences in bulk densities between soils in column studies.

Factors which should be considered, then, in a study of the movement of TCE in soil are the effects of organic carbon content, role of degradation, and effect of flowrate.

MATERIALS AND METHODS

Description of Soils

The two soils used in this study were Chalmers Silty Clay Loam and Russell Silt Loam, both native to Tippecanoe These soils were selected for two main County, Indiana. the soils had sufficiently different organic reasons: contents to allow comparison based upon this carbon parameter; and they are fairly common type soils to many parts of the country as compared to peat, muck, sediment, or extremely sandy soils. The soils are described in detail by the standard nomenclature as reported by the Soil Conservation Service of the U.S. Department of Agriculture (86).

Chalmers Silty Clay Loam

This is one of the most fertile soils in Tippecanoe County and is found in depressions on broad, gently undulating upland till plains in western Tippecanoe County. The soil profile is described as follows (86):

Depth 0-10 inches: very dark gray to black silty loam; relatively high in organic matter; moderate coarse

granular structure; firm when moist: slightly acid to neutral.

Depth 10-15 inches: very dark gray to black silty clay loam; faint yellowish-brown mottling in lower part; coarse granular structure in upper part grades to moderate medium angular blocky in lower part; firm when moist; slightly acid to neutral.

Depth 15-29 inches: mottled gray and yellowish-brown silty clay loam or clay loam; moderate coarse angular blocky structure; very firm when moist; contains dark-gray organic material along the vertical cracks; slightly acid to neutral.

Depth 29-36 inches: mottled gray and yellowish brown loam; contains sand and gravel which may be in thin, slightly stratified layers; moderate coarse to very coarse angular blocky structure; firm when moist; neutral.

Depth 36 inches + : mottled gray and brown loam glacial till; moderately compact; calcareous.

Russell Silt Loam

This soil is extensively found throughout Tippecanoe County. The Russell soil series are found on low knolls and short ridges that slope to a nearly level till plain. The profile is described as follows (86):

Depth 0-7 inches: brown to grayish brown smooth silt loam; low in organic matter; moderate to weak medium granular structure; friable; medium acid to slightly acid.

Depth 11-18 inches: yellowish-brown to dark brown smooth light silt loam; moderate to strong fine subangular blocky structure: slightly firm when moist; medium acid to strongly acid.

Depth 18-28 inches: dark brown or dark yellowish-brown smooth silty clay loam; moderate to strong medium blocky structure; firm when moist, slightly hard when dry; strongly acid to medium acid.

Depth 28-54 inches: dark yellowish brown to dark brown silty clay loam; moderate coarse subangular blocky structures; firm when moist, hard when dry; contains considerable grit and small rock fragments; medium acid to strongly acid in upper part, grading with depth to slightly acid to neutral in the lower few inches.

Depth 54 inches +: brown or pale brown loam to light clay loam glacial till, calcareous.

Soil Sample Collection

Core samples of the soils were obtained with a stainless steel core sampler four feet long having an inside diameter of three inches at the cutting head. The sampler was driven into and removed from the soil with a hydraulically operated soil sampler manufactured by Giddings Machine Company of Fort Collins, Colorado (serial number GSP-M-5-722) which was mounted on a pickup truck chasis For illustration of the sampling rig in operation and a view

of the sampling probe, the reader is referred to Emig (100) and Wentink (22).

A procedure was developed to protect the soil cores from fracture or other disturbance during transport to the laboratory. After removing the sampler from the soil, the cores were extruded from the sampler onto one-half of a 42-inch length of three-inch inside diameter PVC pipe which had been cut in half lengthwise. The other half of the PVC pipe was then placed over the exposed portion of the soil core. Plastic bags were used to cover the end of the cores. The ends and open seams of the pipe were then sealed with duct tape to prevent moisture loss. All soil cores were stored in the pilot plant room of the Civil Engineering building until needed.

All sample cores of the Chalmers and Russell soils were obtained from the Purdue University Agronomy Farm in Tippecanoe County, Indiana. For each soil, all cores were obtained from within an area of approximately 120 square feet. Twenty-eight soil cores of each type of soil were taken to ensure enough cores were available for testing.

Soil Analyses

General

A sample of each profile depth for each soil was air dried and crushed or ground fine enough to pass a No. 10 (2 mm opening) sieve. Approximately 300 grams of each of the

sieved samples were submitted to the Purdue University Soil Characterization Laboratory for the analyses indicated in Table 12.

Table 12. Analyses Conducted by the Soil Characterization Laboratory.

Analysis	Method	Reference	
Cation Exchange Capacity	Sum of Extractable Cations	(64)	
Organic Carbon Content	Meibus	(64)	
Particle Size Distribution	Standard	(64)	
Soil pH	1:1 Water	(64)	

Bulk Density

This test was run in duplicate for each soil profile depth according to the procedures outlined by Black (7) and Purdue University Agronomy Department (64).

Specific Gravity of Soil Particles

Specific gravity was determined on duplicate samples for each soil profile depth according to ASTM method D 854-58 (' and Black (7). These tests were run on soil samples which passed a No. 10 sieve.

Chemical Analyses

pH and Effluent Volume

The pH of the column effluents from the water application phase of the research studies was measured with a Corning Model 125 pH meter which was calibrated each time it was used with a standard pH 7.0 phosphate buffer solution. Effluent volumes were measured and recorded to the nearest milliliter (ml) with a 100 ml graduated cylinder.

Nitrogen

Ammonia nitrogen was determined according to the Phenate Method of Standard Methods (3). This method had a sensitivity of 10 micrograms (ug) ammonia nitrogen/l and was applicable up to 0.5 mg/l. Samples with concentrations greater than 0.5 mg/l were quantitatively diluted prior to analysis. Nitrate nitrogen was measured by the Cadmium Reduction Method of Standard Methods (3). Nitrite nitrogen was determined according to Section 419 of Standard Methods (3).

Chlorides

Chlorides were determined with an Orion Model 96-17 chloride electrode operated from a Model 90 pH/mV meter made by Markson Science, Incorporated. The low level measurement procedure from Orion was used with a low level calibration curve (1.0-48 mg/l) prepared for each sampling run.

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Suspended Solids

Suspended solids were determined with Gelman Metricel Membrane Filters (GA-6), 0.45 micron pore size, according to the following procedure:

- 1. Filters were dried in a 103°C oven for two hours, cooled in a dessicator, and weighed.
- 2. A 100-300 ml volume of filtrate was produced by vacuum filtration.
- 3 Filters and residue were dried for at least two hours in a 103°C oven, cooled in a dessicator, and reweighed.
- 4. A blank filter was processed in the same manner using deionized (DI) water as the filtering solution to correct for any weight gain or loss due to the filter alone.
- 5. Suspended solids were calculated by:

 Concentration $(mg/l) = \frac{\text{Weight gain in filter in mg}}{\text{Volume of filtrate in liters}}$ (17)

Trichloroethylene Analyses

Column Effluent Analysis

Determination of the TCE concentration in the column effluents resulting from the water application phase of the research studies had to be accomplished by a procedure which met the following criteria:

- 1. The procedure had to be readily accomplishable due to the expected number of samples and availability of analytical equipment.
- 2. The procedure had to be able to measure concentrations of TCE in the high mg/l range.

The procedures available for analysis by gas chromatography (GC) included liquid:liquid extraction (LLE), purge and trap, and headspace gas chromatography. LLE using pentane is an accepted, accurate method to quantify TCE in water at the ug/l level (25 32,69,90). It was, however, time consuming and not recommended for levels over 50 ug/l (90). The purge and trap method can be used for TCE (12,42,68,84), but the equipment necessary for this analysis was not available.

Because of the limitations of LLE and purge and trap, headspace gas chromatography (or static headspace analysis) was the method chosen.

Principle: Static headspace analysis is based on the distribution of volatile organics between liquid and gaseous phases. When volatile organics are allowed to come to equilibrium with the vapor headspace in a sealed container, the concentration in the headspace is proportional to the concentration in the water (14,18,44,58,84). The distribution of the organic compounds between the two phases depends upon the effects of vapor pressure, temperature, and ratio of headspace to liquid volume in the container. By keeping

these factors constant, the concentration of the compound in the vapor phase then depends only upon the concentration in the liquid phase (14,18).

Analysis of the headspace gas of the sealed container can allow determination of the aqueous TCE concentration with four major advantages: (1) only relatively volatile compounds readily distribute into the headspace, thereby providing a form of sample cleanup (18); (2) many column and detector contamination problems are eliminated since only gaseous samples are analyzed (14,18); (3) the method can be used for concentrations that vary from the ug/l to the mg/l range; and (4) the method is less time consuming than LLE or purge and trap (18).

GC Operating Conditions. The specific analytical procedure used was modeled after that used successfully by Richter (70) which was adapted from that reported by Dietz and Singley (18). Headspace analyses were conducted using a Varian Model 3700 gas chromatograph with a flame ionization detector (FID) and a CDS 111 data system. Specific GC operating conditions were:

Column Temperature: 90°C

Injector Temperature: 140°C

Detector Temperature: 280°C

Carrier gas flowrate (Nitrogen): 30 ml/min

FID gas flowrate: Hydrogen - 30 ml/min

Air - 300 ml/min

Column: glass 10 ft x 1/4 inch outside diameter x 2 mm inside diameter (Supelco No. 2-3738).

Column packing: 10% SP-1000 on 100/120 Supelcoport as supplied by Supelco.

Retention time of TCE on Column: 2.1 - 2.2 minutes (depending upon condition of column).

All glassware used in the analysis of samples or preparation of standards was cleaned according to the following sequence: detergent wash, tap water rinse, dichromic acid wash, tap water rinse, methanol rinse, DI water rinse, followed by drying at 260°C for at least four hours. Samples were collected in 125 ml (actual capacity 160 ml) serum bottles sealed with Teflon faced septa and aluminum crimp caps. The actual sampling procedure will be discussed in Preliminary Investigations.

Standard solutions were prepared by dilution of Standards. TCE saturated water which had a TCE concentration of 1,100 mq/1. TCE saturated water was prepared by adding approximately 10 ml of TCE (reagent grade as supplied by Aldrich Chemical Co.) to 2.5 liters of DI water in an amber glass continer and stirring with a magnetic stirrer for two The saturated concentrations were periodically compared with standards made by diluting a stock solution of two grams (precise amount determined by weight) of TCE dissolved in 100 ml of methanol. Standard solutions were transferred to 125 ml serum bottles which were sealed with Teflon faced septa and aluminum crimp caps. Thoughout the research, 25 and 50 ml sample volumes were used but the

samples and the standards to which the samples were compared always had the same volume. For each series of analytical determinations a blank of DI water was treated in the same manner as the samples to check the quality of DI water and adequacy of glassware cleaning.

Equilibration: All samples, standards, and blanks were placed on a gyrorotary shaker platform and agitated for 30 minutes prior to analysis. This was determined to be sufficient time for equilibration by tests that were made at five minute intervals during shaking until a stable value was obtained. Others (18,70) used shorter equilibration times, but 30 minutes provided a convenient and satisfactory equilibration period for this research.

Injection: After equilibration, headspace samples were injected into the GC with gastight syringes (Hamilton 1000 series, 0.25 or 0.5 ml capacity). The usual injection volume was 0.25 - 0.50 ml with the 0.5 ml syringe reserved for low concentrations and the 0.25 ml syringe reserved for high concentrations. TCE concentrations were calculated by comparing the GC response for the sample to that of the standard with the following equation:

TCE concentration =

F x TCE conc. in std. x (mean peak area of sample) (mean peak area of std.) (18)

Where F = injection volume of standard injection volume of sample

The mean peak area was the mean of peak areas from three injections in which the largest response was less than 10% greater than the smallest response.

Between injections, the needle and plunger were removed from the syringe. The barrel was attached to a vacuum pump and purged for approximately two minutes. Periodically, an aliquot of room air was injected to check syringe cleanliness.

Two or three standards were used for each analysis run as a check on linearity and to ensure that the range of sample concentrations was within those of the test samples being measured. The procedure gave a linear response up to 880 mg/l as shown by Table 13 and the example calibration curves of Figure 2. Consequently, for sample concentrations greater than 800 mg/l, the samples were diluted prior to analysis.

Temperature effects were minimized by keeping all samples and standards in the same location (approximately 18-22°C) during GC injection.

The possible loss of TCE through pierced septa was of concern although Dietz and Singley (18) found such loss insignificant. This investigation found no discernible loss from standards injected at the beginning of a series of analyses compared to injection of the same standards at the end of the same series of analyses. This was true even though, during the three to four hour elapsed time, the

Table 13. GC Linearity Data for Headspace Analysis.

TCE Conc., mg/l	Mean Peak Area, units	r ²	Sample Volume, ml	Injection Volume, ml	Range
0.011 0.055 0.110 0.220 0.440 0.660 0.880 1.100	6,309 22,465 57,621 119,862 221,312 310,861 419,754 578,605*	0.983	50	0.50	10-12
1.1 11 55 110 220 440 660 880 1100	456 4,510 21,695 44,383 86,041 168,781 259,668 336,135 566,152*	0.988	50	0.25	10 - 9
55 110 220 440 660 880 1100	14,698 29,101 61,965 118,757 179,414 242,412 392,145*	0.996	25	0.25	10-9

Note: Values marked with * not included in regression to determine r^2 .

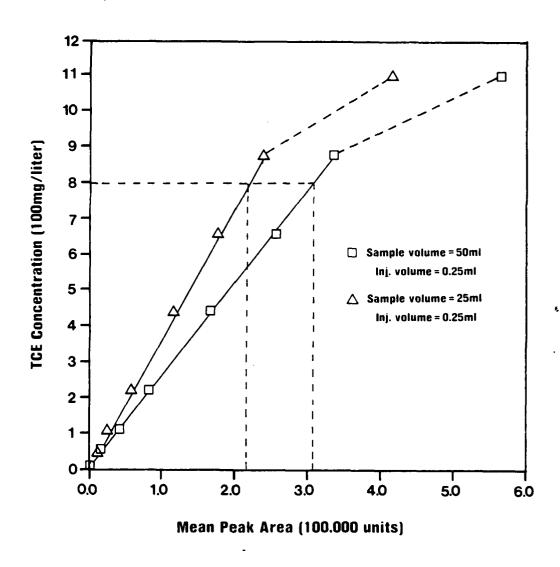


Figure 2. GC Response for Different Sample Volumes.

septum may have been pierced up to five times. Regardless, to minimize any such loss, each sample was injected as soon after equilibration as possible. Usually, analyses were complete within four hours after sample collection.

The effects of sample matrix and variation of sample volume will be discussed in Preliminary Investigations.

Soil Sample Analysis

This procedure was adopted from an article by DeLeon et al. (16) using the operating conditions reported by the U.S. Environmental Protection Agency (90).

Sample Collection. The glass column and the soil core it contained were placed in a refrigerated room maintained at 4°C. The top stopper was removed from the column and an airline was connected to the glass tube that pierced the bottom stopper in the column. Using a slight air pressure, the soil core was extruded from the column onto a 42-inch section of 3-inch inside diameter PVC pipe cut in half lengthwise. The half section of pipe had been previously lined with alumunum foil. Samples of the soil were taken from several different locations within a particular profile depth. The individual samples were mixed together on an aluminum foil covered base to form a composite sample for that depth.

Extraction. Approximately two grams of the composite soil sample were transferred to a tared 6 0 ml Hypovial (actual capacity 11 ml; Pierce Chemical Co.) and weighed. Six ml of

n-pentane (reagent grade redistilled in glass) were added to the vial which was then sealed with a Teflon faced septum and aluminum crimp cap. The exact amount of pentane added was determined by weight. The sealed vial was then placed on a vortex mixer for 60 seconds and stored in a freezer at -15°C until analyzed. In no case was the sample held for longer than 10 days prior to analysis.

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Dry Weight Determinations. A 20-25 gram portion of each soil sample was placed in a tared aluminum weighing boat and weighed. The sample was then dried in a 103°C oven for 24 hours, cooled in a dessicator, and weighed to determine weight loss due to water content. The percent water content was used to correct the extracted soil samples to a dry weight basis.

GC Operating Conditions. Analysis was conducted with a Varian model 3700 gas chromatograph with a 63 Ni foil electron capture detector (ECD) and a CDS 111 data system. Specific GC operating conditions were:

Column Temperature: 65°C

Injector Temperature: 110°C

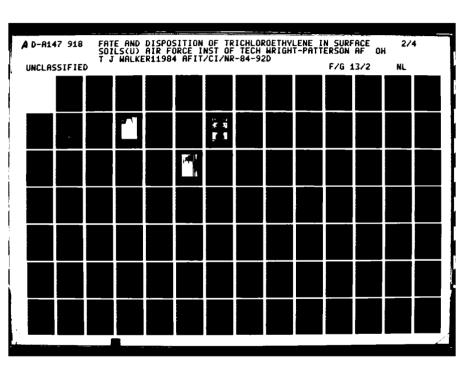
Detector Temperature: 240°C

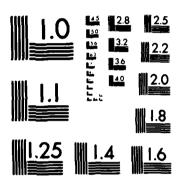
Carrier Gas Flow Rate (N2): 30 ml/min

Column: Glass, 6.0 ft x 1/4 inch outside diameter x 2.0 mm inside diameter (Supelco No. 2-1721).

Column Packing: 10% Squalene on 80/100 Chromosorb WAW as supplied by Supelco.

Sample Size: 2-6 microliters.





MICROCOPY RESOLUTION TEST CHART
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Retention Time of TCE on Column: 1.9 minutes Detector Sensitivity: 10^{-11} or 10^{-12} amp/mV (ECD 10 or 1).

Between injections, the microsyringe was flushed with pentane. Periodically, pure pentane was injected to ascertain syringe cleanliness.

Sample Recovery and Calculation. Based upon absolute standards of TCE in pentane, a series of spiked soil samples was used to test the recovery of the method. For each soil type, a composite soil mixture was made by mixing quantities of dry soil from each profile in proportion to the dry weight of the soil profile. Two grams of the composite sample were placed in a tared Hypovial, weighed, and sealed. The water content of the soil was adjusted to 20% by injecting the appropriate quantity of DI water through the septum, weighing to verify the amount of water, and mixing on a vortex mixer. The soil was spiked by injecting TCE with a microliter syringe. The vial was then reweighed to determine the amount of injected. Pentane was injected into the vial, the vial was reweighed, and the spiked samples analyzed regular Table 14 lists the recoveries for concentrations of spiked samples.

82.2

Chalmers Composite Soil			site Soil	Russell Composite Soil		
TCE	Conc.	(ug/g)	% Recovery	TCE Conc.(ug/g)	% Recovery	
-	190		60.3	233	63.2	
	254		68.2	309	71.6	
	580 807		86.6 82.1	726 806	73.8 80.1	
	929		74.2	1007	69.9	

Table 14. TCE Recovery from Composite Soil Samples.

Generally, the lower concentrations had lower recoveries. To minimize error introduced by poor recoveries, unknown samples were compared to spiked standards instead of to absolute standards. Concentrations were calculated on a soil dry weight basis by:

1170

Concentration = Peak area of sample (ug TCE/g Soil) = Peak area of std.

70.3

1155

Where F = <u>Injection volume of standard</u> Injection volume of sample

M = Dry mass of soil used in extraction, g
Mass of pentane used in extraction, g

Peak Area = Mean peak area of three injections with the largest no more than 10% greater than the smallest.

Adsorption Isotherms

Soil

Isotherms were developed for coarse and fine particle sizes of soil. To obtain the coarse particle size soil, a

quantity of soil was ground with a mortar and pestle until all of that quantity of soil passed a No. 10 sieve (<2 mm). To obtain the fine particle size soil, a quantity of coarse particle size soil was ground in an electric carbon grinder, then further ground with a mortar and pestle until all of the soil passed a No. 100 sieve (0.150 mm opening). All soil was autoclaved for two hours to minimize any possible biodegradation losses during testing. All soil was dried at 103°C for four hours and cooled in a dessicator prior to weighing the aliquots of 10 g. The basic procedure was based upon methods used in the literature (4,7,32,69,100). The following specific steps were followed with initial TCE concentrations of 110 - 1,100 mg/1:

- l. Pour approximately 10 ml of TCE solution into a
 glass liquid scintillation vial (actual capacity 25 ml) from
 a full 25 ml graduated cylinder.
- 2. Immediately, add the preweighed aliquot of 10 grams of soil to the vial.
- 3. Place a Teflon faced septum on the vial, hold in place by hand, and gently tap and invert the vial several times to release entrained air.
- 4. Fill the vial with solution and record the total volume of solution used.
- 5. Immediately replace the septum to eliminate headspace and tightly seal the vial with an open screw cap.

- 6. Seal all vials in a carton to minimize exposure to light and equilibrate on a shaker table at 20°C for 48 hours.
- 7. After 48 hours, remove vials and centrifuge at 8,000 rpm for 20 minutes in a refrigerated room (4°C).
- 8. Withdraw an aliquot of clarified solution through the septum with a syringe and dilute to 25 ml in the syringe.
- 9. Inject sample into a sealed serum bottle for GC analysis.

During the equilibration period, the vials were inverted on the shaker table six times daily to provide additional mixing. For each different initial TCE concentration, duplicate adsorption vials were used. The results were calculated from the averages of the mass of soil, volume of solution, and final TCE concentration within the two vials. To correct for volatilization losses, duplicate blanks (scintillation vials without soil added) were processed in the same manner except step 2 was eliminated. Results were calculated as follows:

1. Volatilization loss, VL, %

$$VL = \frac{C_{i} - C_{b}}{C_{i}} \times 100\%$$
 (20)

Where C_i = initial TCE concentration.

2. TCE adsorbed, X

$$X = (C_b - C_f) \times V \tag{21}$$

Where C_f = Final average TCE concentration in adsorption vials after equilibration.

V = Average volume of TCE solution used in adsorption vials.

Adsorptive capacity, q.

$$q = X/M \tag{22}$$

Where M = Average mass of soil in adsorption vials.

Glass and Gravel

The adsorptive effects of glass and gravel were studied in separate experiments with inital TCE concentrations of 110-1,100 mg/l. Glass adsorption tests used four mm diameter glass beads which had been acid washed, rinsed, and dried at 260°C for 24 hours. Gravel adsorption tests used 1/4 - 3/8 inch gravel which had been washed to remove silt and dried at 260°C for 24 hours. The procedure was as follows:

- 1. Pour approximately 50 ml of TCE solution from a full 250 ml graduated cylinder into a 125 ml serum bottle.
- 2. Immediately, add the preweighed sample of 75 grams of glass or 70 grams of gravel to the bottle.
- 3. Place a Teflon faced septum on the bottle, hold in place by hand, and gently tap and invert the bottle several times to release entrained air.
- 4. Fill the bottle with solution and record the total volume of solution used.

- 5. Immediately replace the septum so as to eliminate headspace, then seal with an aluminum crimp cap.
- 6. Seal all bottles in a carton to mimize exposure to light and place in a 20°C laboratory area for 72 hours.
- 7. After 72 hours invert the bottle several times to mix. Withdraw an aliquot of solution of 25 ml or less through the septum with a syringe. For aliquots less than 25 ml, dilute to 25 ml in the syringe with DI water.
- 8. Inject 25 ml sample into a sealed serum bottle for GC analysis.

During the equilibration period, the bottles were inverted three times daily to provide mixing. For each initial TCE concentration tested, a blank without glass or gravel was processed in the same manner except step 2 was eliminated. X/M values were calculated in the same manner as those for soil adsorption. Adsorptive capacity based on glass surface area was as calculated in Appendix A.

Warburg Respirometry Studies

These studies were conducted to determine the relative rates of aerobic biodegradation of TCE by various soil profiles. The respirometric technique is based on the principle that oxygen consumption in a closed system is indicated by a pressure change which can be measured by micromanometers. This pressure change can then be converted into a volumetric determination of oxygen consumed when the

corresponding carbon dioxide produced is absorbed by a solution of KOH.

The Warburg Respirometer is commonly used to measure oxygen consumption in aerobic liquid cultures. Its use in these studies was adapted from accepted methods for liquid cultures based upon Umbreit et al. (85). The specific procedure was:

- 1. Add 0.2 ml of 10% KOH solution to the center well of a flask and insert a fluted filter paper wick.
- 2. Add 2.0 ml of air dried, coarse particle size soil (pass No. 10 sieve). (The 2.0 ml was determined by weight based upon the specific gravity of soil particles for that profile).
 - 3. Attach flask to the proper matched manometer.
- 4. Equlibrate flask at 25°C for 10 minutes with manometer vents open.
- 5. Add 1.0 ml of substrate to sidearm of flask and close stopcock.
- 6. In five minutes, adjust level of manometer fluid in closed end of manometer to 250 mm and read level of fluid in open end. Use this reading as zero time reading.
 - 7. Tip in substrate from sidearm.
- 8. At appropriate time intervals, read pressure change on manometer by readjusting level in closed end to 250 mm and recording the level in the open end.

The temperature of the water bath was held constant at 25°C during the studies. The change in barometric pressure accounted for with a blank flask called thermobarometer. Glucose solution, TCE solution and TCE solution with added ammonia were used as substrates. DI water was used as an endogenous control substrate. All solutions were adjusted to pH 6-7 before use. Each different substrate and concentration of substrate was run in either duplicate or triplicate.

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Individual manometer readings were corrected for atmospheric pressure changes then converted to oxygen uptake by the following relationship:

$$O_2$$
 uptake, ul = k x h (23)

Where k = flask constant, ul/mm manometer solution, specifically determined for each
flask and corresponding manometer.

h = corrected change in manometer fluid height from previous reading.

The individual oxygen uptake calculations were summed to provide a total cumulative oxygen uptake over the duration of the test. The total cumulative oxygen uptake quantities were then averaged for the duplicate or triplicate measurements. An average exogenous uptake was then calculated by subtracting the average endogenous uptake from the average total cumulative oxygen uptake for each test.

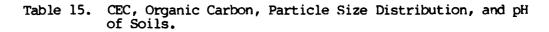
PRELIMINARY INVESTIGATIONS

Prior to initiation of column studies, techniques, procedures, and methods were investigated to develop a satisfactory experimental protocol for the studies. Included in these investigations were soil methods and rates of water analyses, column setup, methods of effluent collection, application, sample extraction, effects of sampling on GC analysis for TCE, and TCE application to the soil columns.

Soil Analyses

The results of initial soil analyses are presented in Tables 15 and 16. Tables 16 and 17 also contain some soil parameters calculated according to Appendix A.

General observations showed that the bulk density of the soil and the specific gravity of the soil particles increased with depth while the porosity and organic carbon content decreased with depth. This is typical of most soils because the organic matter is generally associated with porous structures which are less dense than discrete particles of silt or clay (2). Additionally, the burden of overlying soil generally compacts the deeper subsurface



Soil Depth,	CEC,	% Organic		le Size	Dist. %	Textura	l pH
	eq/100g	Carbon	Clay	Silt	Sand	Class	
Chalmers Soi	1						
0-10	26.4	3.03	25.8	57.6	16.6	SiL	6.1
10-15	26.1	1.33	21.6	67.9	10.5	SiL	6.2
15-29	28.4	0.59	30.9	60.9	8.2	SiCL	6.5
29-33	18.1	0.32	35.0	62.4	2.6	SiCL	7.2
Russell Soil							
0-7	12.2	1.22	23.6	67.0	9.4	SiL	6.5
7-11	20.0	0.49	13.2	78.6	8.2	SiL	6.4
11-18	19.5	0.41	22.2	73.5	4.3	SiL	5.4
18-28	16.5	0.36	27.4	72.0	0.6	SiCL	7.0
28-33	18.3	0.23	29.3	67.1	3.6	SiCL	5.0

Table 16. Physical Parameters of Soils.

Soil Depth, inches	Bulk Dens g/cm ³	ity, ρ	n	Calculated Bulk Volume, cm ³	Calculated Pore Volume, cm ³
Chalmers Soi	1				· — —
0-10	1.31	2.50	0.476	1,158	553
10-15	1.44	2.54	0.434	579	252
15-29	1.46	2.57	0.433	1,620	703
29-33	1.48	2.58	0.425	463	198
Total	1.41		0.446	3,820	1,706
Russell Soil	<u>.</u>				
0-7	1.37	2.53	0.458	810	371
7-11	1.40	2.55	0.451	463	209
11-18	1.50	2.58	0.418	810	339
18-28	1.54	2.59	0.405	1,158	469
28-33	1.56	2.58	0.396	579	229
Total	1.48		0.423	3,820	1,617

Notes: 1. ρ = Specific gravity of soil solids (unitless). 2. n = Calculated porosity (unitless). 3. Calculations made according to Appendix A.

Table 17. Calculated Soil and Organic Carbon Mass.

Soil Depth, inches	Calculated Soil Mass, g	% of Total Mass	% Organic Carbon	Calculated Organic Carbon Mass, g
Chalmers Soi	.1			
0-10	1,517	28.1	3.03	46.0
10-15	834	15.4	1.33	11.1
15-29	2,365	43.8	0.59	14.0
29-33	685	12.7	0.32	2.2
Total	5,401	100.0	1.4	73.3
Russell Soil	<u>.</u>			
0-7	1,110	19.6	1.22	13.6
7-11	648	11.5	0.49	3.2
11-18	1,215	21.5	0.41	5.0
18-28	1,783	31.4	0.36	6.4
28-33	903	16.0	0.23	2.1
Total	5,659	100.0	0.53	30.3·
			· · · · · · · · · · · · · · · · · · ·	·····

Notes: 1. Calculations made according to Appendix A. 2. Percent organic carbon measured by Soils Characterization Laboratory.

soils causing the porosity to decrease with depth (7). Compared to the Russell soil, the Chalmers soil showed a higher organic carbon content and slightly lower bulk density for corresponding profile depths. There appeared to be no discernible correlation between neither CEC and organic carbon content nor CEC and clay content for either soil.

Soil Column Setup

The technique used by Wentink (100) and Emig (22) for operation of their soil columns was the basis for the leaching method developed for these investigations. Since Wentink and Emig both studied nonvolatile compounds, their setup was modified for use with TCE as shown in Figure 3. The columns were assembled in the following manner:

- 1. Place a 38-inch length of glass tubing (Corning No. 234850-7740 Pyrex Standard Wall Tubing; 80mm inside diameter; 85mm outside diameter) in a horizontal V-shaped trough eight feet long.
- 2. Remove half of the PVC pipe soil core container and strip away all tape and plastic bags. Crop the grass and vegetation closely to the soil surface.
- 3. Place the soil core container on the trough with the surface end of the core butted snugly against the glass tubing.

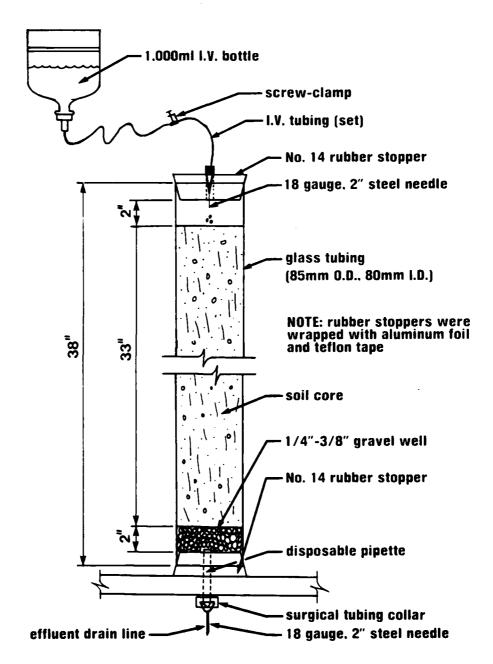
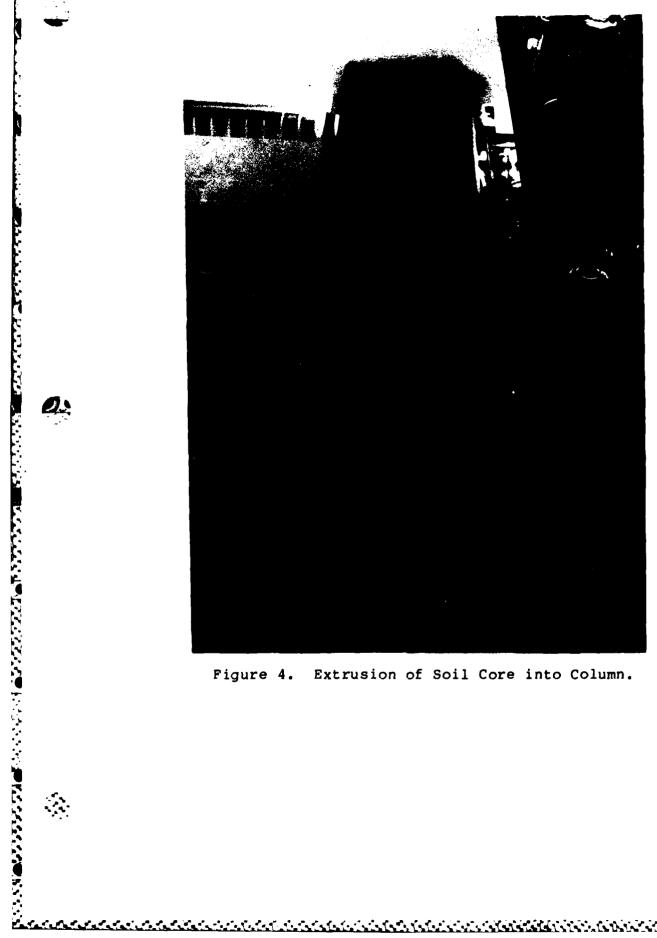


Figure 3. Diagram of Soil Column.

- 4. Gently push the soil core into the tubing while carefully monitoring the integrity of the core (see Figure 4).
- 5. When 33 inches of soil are in the tubing, trim the core squarely with the end of the tubing, then gently push the core three inches farther into the tubing.
- 6. Insert a three inch thick spacer (to hold column in place) into the top end of the tubing, turn the column upside down into a vertical position and place two inches of 1/4-3/8 inch gravel in the bottom of the column.
- 7. Tightly seal the column bottom with a No. 14 rubber stopper prepared for sample collection.
- 8. Turn the column upright, remove the plug and place column in the support rack. Tightly seal the top with a No. 14 one hole rubber stopper which has been wrapped with aluminum foil and non-reactive Teflon tape to minimize adsorption onto the stopper.

The stopper used to seal the bottom of the column was assembled to provide for sample collection. A No. 14 one hole rubber stopper was wrapped with aluminum foil and non-reactive Teflon® tape. A 5-3/4 inch disposable glass pipette with the fine tip removed by grinding was inserted through the stopper hole as shown in Figure 3.



Extrusion of Soil Core into Column.

Approximately 1/8 inch of the pipette extended into the gravel bed with the stopper in place. With the column in the rack, an 18 gauge, two-inch steel syringe needle was used to cover the tapered end of the pipette. The needle was held in place with a 1/2 inch collar of surgical tubing as detailed in Figure 3.

Preliminary studies conducted with test columns assembled without a gravel bed proved unsatisfactory because the columns drained poorly, the needle frequently clogged, and cloudy effluents with 6.0-10.0 mg/l suspended solids were produced. Since there was concern the solids could interfere with TCE analysis, gravel was added to the column to serve as a porous base to improve drainage as recommended by Hamaker (30). With gravel, test columns produced clear effluents with suspended solids less than 1.0 mg/l.

Column headspace was limited to approximately two inches. This depth was large enough to allow visual inspection of water application but not too large to allow excessive TCE volatilization.

The 33 inch length of soil was chosen based on several factors. This length spanned the upper soil profiles with varied physical and chemical parameters. Below 33 inches, the characteristics of the soil changed only slightly. Additionally, below 33 inches, the soil cores were fragile and easily split or broke, thus disturbing their integrity.

Effluent Collection

Procedure

All water leached through the columns was collected and is hereafter referred to as column effluent. The way in which the effluent was collected depended upon whether or not the TCE concentration was to be determined for that particular sample. For samples in which TCE was not determined, effluent was collected by placing a serum bottle beneath the column as shown in Figure 5. All analyses other than TCE used effluent collected in this way.

Samples for TCE analysis had to be collected in a manner which would eliminate or, at least, minimize TCE loss by volatilization. Schwarzenbach and Westall (77) used an evacuated syringe to collect column effluent for volatile organic analysis. A modification of this approach was tried with some preliminary test columns by attaching a glass syringe to the effluent drain. A sample was withdrawn with the syringe but the vacuum was enough to produce a cloudy effluent. Also, unless the effluent drain were restricted, insufficient sample accumulated in the gravel bed to collect the needed sample volume. Consequently, this method was unsatisfactory.

The method developed for use was similar to that of Schwarzenbach and Westall (77) except an evacuated 125 ml serum bottle was used instead of an evacuated syringe. A serum bottle was sealed with a Teflon faced septum and



Figure 5. Collection of Sample without TCE Analysis.

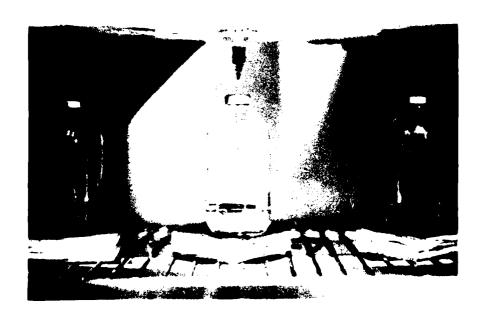


Figure 6. Collection of Sample with TCE Analysis.

aluminum crimp cap. The bottle was then partially evacuated through a syringe needle which pierced the septum and was connected to a vacuum pump. The approximate vacuum was determined by a gauge in the vacuum line. The necessary vacuum was determined in a series of tests in which serum bottles were evacuated to different absolute pressures. The septa of these bottles were then pierced with a needle attached to a 50 ml syringe barrel filled with water. Based upon the amount of water which was sucked into the bottle, the degree of vacuum was chosen which would collect the desired sample volume. This vacuum was then used to prepare subsequent sample bottles.

After the serum bottle was evacuated, it was attached to the effluent drain line by piercing the septum as shown in Figure 6. Effluent was slowly collected in the bottle as it reached the bottom of the column. Effluent was generally collected overnight.

All serum bottles used for TCE analysis were permanently marked at the 25 and 50 ml levels so sample volumes could be easily identified. If the volume of the sample was greater or less than the volume desired, the sample volume was adjusted in the following manner:

1. If the sample volume was greater than 25 ml and the expected sample concentration was greater than 800 mg/l, the sample was diluted to the 50 ml mark by injecting DI water with a graduated syringe and needle into the bottle through the septum.

- 2. If the volume collected was greater than 25 ml, but the sample concentration was expected to be less than 800 mg/l, the sample was withdrawn with a syringe and needle until the liquid level reached the 25 ml mark. During sample withdrawal, an empty needle was inserted through the septum and extended to about 0.5 inches below the liquid level in the bottle. This needle allowed an equal volume of air to replace the volume of liquid withdrawn, since the pressure in the headspace was able to stay at a constant level because of the balance between liquid levels and pressures in the bottle. If analysis proved the concentration was greater than 800 mg/l, the sample was diluted to 50 ml as in Step 1.
- 3. If the volume of sample collected was less than $25\ \text{ml}$ and sample concentration was expected to be less than $800\ \text{mg/l}$, the sample was diluted to $25\ \text{ml}$ as in Step 1.
- 4. In all cases, the amount of sample withdrawn or the amount of dilution water added was recorded.

 In this way the exact amount of the effluent was determined by the volume differential in the sample collection bottle.

Regardless of the manner in which samples were collected, or diluted for analysis, all effluent from the

columns was collected and accounted for except that possibly lost to evaporation. To estimate evaporative loss, 100.0 ml of DI water were poured into an open serum bottle and placed in the 20°C room where the columns were housed (hereafter referred to as the column room). After 24 hours, the water was poured into a graduated cylinder and the volume was measured as 99.6 ml. This slight loss was considered negligible and, consequently, evaporative loss of effluent from unsealed serum bottles was not further considered.

TCE Volatilization Loss During Sample Collection

In Materials and Methods, the possible loss of TCE through pierced septa during analysis was discussed and reported to be an insignificant factor. Another source of anticipated volatilization loss was leakage around the column needle piercing the bottle septum during sample collection. To investigate this loss, a series of standards with TCE concentrations of 110-880 mg/l was analyzed in the following manner:

- 1. Prepare a set of four identical standards in serum bottles for each concentration. Place two of the bottles from each set in the column room.
- 2. To simulate the hole used for evacuating the sample bottle, pierce the septa of the remaining two bottles of each set with an empty syringe needle. Then, insert into each of the septa an 18 gauge, 2-inch syringe needle which is fitted with a

glass rod, held in place with a collar of surgical tubing. This simulates the column needle which pierces the septa during sample collection.

- 3. Place the pierced bottles in the column room and ensure the needles remain upright.
- 4. After 24 hours, remove needles and analyze all four bottles of each set for TCE as compared to freshly prepared standards.

The results of this test are shown in Table 18. appears to have been a slight loss of TCE from both the pierced and unpierced septa when considering the entire concentration range tested. However, the maximum loss was 5.3%, with test concentrations greater some corresponding fresh standards. This indicated there could have been some variation due strictly to experimental error and slight differences in preparing standards. Additionally, the test was run for 24 hours while the sample bottles were to be connected for only 12-16 hours. The levels of volatilization loss were considered negligible and not accounted for in subsequent testing.

Variation in GC Response

Effects of Sample Matrix

The accuracy of TCE analyses was of some concern since the GC response of the effluents was compared with GC response of standards prepared in DI water. To study the

Table 18. Loss of TCE through Pierced Septa.

Standard	Unpierced Septa		Pierced	Pierced Septa	
TCE Conc., mg/l	TCE Conc., mg/l	% of Std.	TCE Conc., mg/l	% of Std.	
110 220	106 213	96.4 97.0	113 208	102.7 94.7	
440 660	452 628	102.7 95.2	443 637	100.7 96.5	
880	897	101.9	856	97.3	
Mean Standard Deviation		98.64 3.415		98.38 3.251	

Sample Volume = 25 ml; Injection Volume = 0.25ml; Range = 10^{-9} .

Table 19. Variation in FID Response Due to Sample Matrix.

			Mean Peak	Area	
TCE Concentration	on, DI Water	Chalmers Effluent	% of DI Response	Russell Effluent	% of DI Response
110 220 440 660 880 r ²	27,519 61,099 122,461 169,472 254,543 0.990	26,418 59,938 124,665 164,727 246,652 0.983	96.0 98.1 101.8 97.2 96.9	28,537 61,649 119,644 172,353 253,016 0.978	103.7 100.9 97.7 101.7 99.4
Mean Standard Dev	viation		98.0 2.253		100.68 2.276

Sample Volume = 25 ml; Injection Volume = 0.25ml; Range = 10^{-9} .

effects of sample matrix, effluent from several uncontaminated test columns of both soil types was collected. A portion of each type of effluent was saturated with TCE. TCE saturated effluent was then diluted with uncontaminated effluent to provide standard concentrations in the range of 110-880 mg/l. These standards were analyzed and compared to standards made with DI water. Results of the comparison are shown in Table 19.

Singley (18)had found Dietz and that salt concentrations up to 1.0% significantly increased the GC response of TCE concentrations in the few ug/l range. this study, there were only slight variations in response to sample matrix. The responses of the effluent standards were all within + 4.0% of the corresponding DI standards. This level of variation was considered less than necessary to justify preparation of standards with column effluents. Consequently, all further analyses were quantified with standards prepared with DI water.

Effects of Sample Volume

Since the liquid volume in the serum bottles was to be determined from permanent side markings, there was some concern that the accuracy of determining the liquid volume could affect the accuracy of the analysis. Determination of the sample volume by the meniscus of the liquid level in the bottle at the marking was accurate to within \pm 0.5 ml. To determine the GC response with slight variations in sample

volume, a series of standards from 110-880 mg/l TCE were analyzed with volumes of 24,25, and 26 ml. The results are shown in Table 20 and Figure 7. As expected, the 24 ml sample volume generally produced a lower GC response than did the corresponding 25 ml sample volume. Conversely, the 26 ml volume generally produced a higher reponse than the 25 ml volume. In all cases, however, the responses were within ± 3.0% of the responses for the 25 ml sample volume. Consequently, the effect of sample volume was considered no further.

Application of Water To Columns

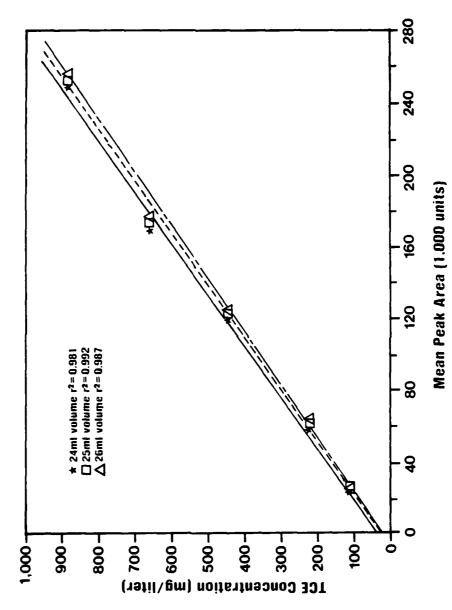
Water was applied to the columns with the same application scheme used by Wentink (100) and Emig (22) which was shown in Figure 3. Deionized water, with the pH adjusted to 5.5-6.0 with 0.1N sulfuric acid when necessary, was placed in a 1,000 ml intravenous (IV) feed bottle to which IV tubing with a screw clamp was attached. delivery end of the tubing was connected to a two-inch 18 gauge steel syringe needle which was then inserted into the hole in the top stopper of the column. The screw clamp and needle sufficiently restricted flow through the tubing to allow the desired daily application rates. Flowrate was adjusted by tightening or loosening the screw clamp.

Application rates were determined on the basis of the quantity of water which could be applied to the columns on a

Table 20. Variation in FID Response with Sample Volume.

TCE Conc.,	24 ml	Volume	25 ml		26 ml Volume
mg/1	мра	% of 25 ml MPA	MPA	MPA	% of 25 ml MPA
110	24,866	97.6	25,473	25,229	99.1
220	58,962	97.8	60,302	60,994	101.1
440	119,021	97.1	122,563	123,947	101.2
660	169,974	97.3	174,690	178,941	102.4
880	249,334	99.2	251,345	255,367	101.6
r ²	0.981		0.982	0.978	
Mean		97.8			101.1
Standar Deviatio		0.851			1.22

Note: 1. MPA = Mean Peak Area



Variation in FID Response with Different Sample Volumes. Figure 7.

daily basis and not cause ponding on the top of the columns. Ponding was undesirable because it could clog surface pores, cause anaerobic conditions within the soil columns, and upset the leaching conditions desired in the study. To determine the maximum application rates, a set of test columns of each soil were leached with DI water at rates of 50-200 ml/day. From these tests, it was found that water applied at 125 ml/day or more caused ponding. Consequently, the maximum daily water application rate was chosen as 100 ml/day with a secondary rate of 50 ml/day. In terms of rainfall, these application rates for a three-inch diameter soil core were:

50 ml/day = 1.10 cm/day = 0.43 inches/day

100 ml/day = 2.20 cm/day = 0.86 inches/day

Flowrate was adjusted daily, based upon amount of effluent collected.

Application of TCE to Soil

Since the purpose of this study was to investigate the movement of TCE through soil as a result of a spill, it was necessary to make a reasonable estimate of the quantity of TCE to apply to soil columns. As a basis for this estimate, the $K_{\rm D}$ for TCE was calculated from Equation 8:

$$K_p = (0.63)(195)(f_{OC})$$

=123 x f_{OC} (on a gram/gram basis)

Assuming a linear adsorption isotherm of Equation 4,

$$X/M = (123) (f_{OC})(C)$$

When X/M is expressed in mg/g and C is in mg/l, K_p becomes:

$$K_p = (123 \text{ g/g})(f_{oc})(1 \text{ liter/1000g})$$

$$= (0.123 \text{ 1/g})f_{OC}$$

Then,

$$X/M = 0.123 \times f_{OC} \times C$$
 (22)

This equation was used to calcuate the values shown in Table 21. Since at this point in the research the organic carbon content of the soils had not yet been determined, f_{OC} was estimated based upon similar soils. It was also assumed that water leaching through the columns would reach a concentration of 1,100 mg/l, the maximum solubility of TCE. Based upon these calculations, the maximum amount of TCE that would be adsorbed on the columns was 7.31 g (5.0 ml) on Chalmers soil and 3.83 g (2.62 ml) on Russell soil.

Table 21. Calculated TCE Adsorption.

Parameter	Chalmers Soil	Russell Soil
Estimated foc	0.01	0.005
Total Soil Mass, M	5,401 g	5,659 g
<pre>X/M, mg/g at C = 1,100 mg/1</pre>	1.353	0.677
TCE Adsorbed, X	7.31 g	3.83 g
TCE Adsorbed, X	5.01 ml	2.52 ml

These calculated values were gross estimates since the valid range for Equations 4 and 8 were greatly exceeded.

Additionally, it was recognized that portions of the TCE applied to the columns might be lost due to degradation and volatilization, thus increasing the amount which could be applied without exceeding the adsorptive capacity of the soil. However, since the TCE was to be applied directly to the soil instead of in solution, the adsorptive capacity of the soil was expected to be higher than that calculated in Table 21. Considering these factors, the TCE loadings chosen for study were 5.0 ml and 10.0 ml on each soil column. Comparative loadings are indicated below:

5 ml/col = 7.3g/col = 0.054 gal/ft² = 0.043 inches/column
10 ml/col = 14.6g/col = 0.108 gal/ft² = 0.086 inches/column
For ease of analysis, and to eliminate interference due to impurities, reagent grade TCE, which had been redistilled in

Initiation of Column Studies

glass, was used to dose the columns.

Thirteen soil columns of each soil type were assembled, placed in support racks, and plumbed to ensure the columns were vertical. The columns were located in a 20°C temperature controlled room (column room) as shown in Figure 8. All columns were saturated with DI water then allowed to drain until no further drainage occurred (all columns ceased draining after 48 hours). To apply TCE, the top stopper of the column was removed and 5.0 or 10.0 ml of TCE (according to Table 22) were applied to the surface of the soil core with a volumetric pipette. The stopper was immediately

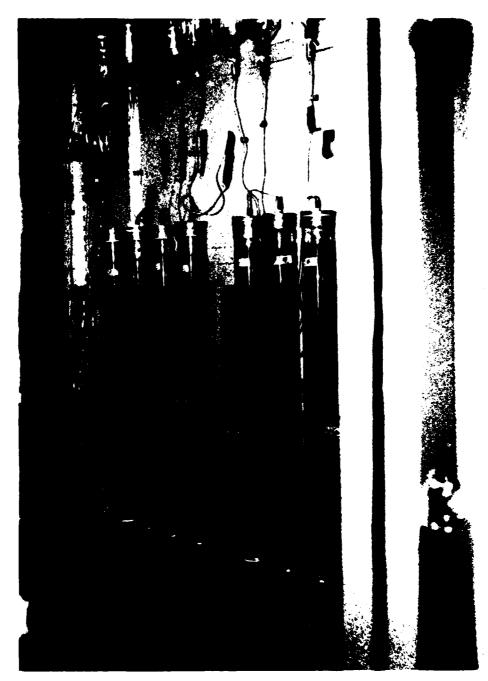


Figure 8. Column Study Assembly.

replaced to tightly seal the column. To maximize adsorption of the TCE, no water was applied for 24 hours. After 24 hours, water was applied according to the schedule of Table 22. The day water application began was logged as Day 0, with the first attempt to collect effluent listed as Day 1, according to Appendix B.

One soil column of each soil type was not dosed with TCE but was leached with water as a control column. Il conditions were run with triplicate columns so that any fluctuations due to a particular column could be compensated for by the response of other similar columns.

For convenience of discussion and as a basis for comparison, the typical laboratory day during the column studies was conducted according to the following approximate time schedule, beginning with Day 1:

1. 6-7:30 A.M.: Removed sample bottles from columns scheduled for TCE analysis and replaced evacuated bottles with open serum bottles to collect any additional effluent during the day. Prepared samples for analysis and recorded sample volumes as well as all effluent volumes collected. To be consistent, all effluent collected during the previous 24 hours (including sample) was recorded as of the morning the volume was determined. Any additional effluent or sample collected later during the day was recorded for the following day.

Table 22. Operating Conditions for Column Soil Studies.

Chalmers Soil 5.0 50 C2 5.0 50 C3 5.0 50 C4 5.0 100 C5 5.0 100 C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 100 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 R2 5.0 50 R3 5.0 100 R4 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100 R11 10.0 100 R12 10.0 100 R9 10.0 100 </th <th>Column Number</th> <th>TCE Applied, ml</th> <th>Water Application Rate, ml/day</th>	Column Number	TCE Applied, ml	Water Application Rate, ml/day
C1 5.0 50 C2 5.0 50 C3 5.0 50 C4 5.0 100 C5 5.0 100 C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 50 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	Chalmers Soil		
C2 5.0 50 C3 5.0 50 C4 5.0 100 C5 5.0 100 C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 50 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100		5.0	50
C4 5.0 100 C5 5.0 100 C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 100 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100			50
C5 5.0 100 C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	C3	5.0	50
C6 5.0 100 C7 10.0 50 C8 10.0 50 C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 Russell Soil 50 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	C4	5.0	100
C7	C5	5.0	100
C8 10.0 50 C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 Russell Soil 50 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	C6	5 . 0	100
C9 10.0 50 C10 10.0 100 C11 10.0 100 C12 10.0 100 CC (Control) 0.0 100 Russell Soil 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 50 R9 10.0 100 R10 100 R10 100 R11 10.0 100	C7	10.0	50
C10 10.0 100 100 C11 100 C12 10.0 100 CC (Control) 0.0 100 CC (Control) 0.0 50 F2 5.0 50 F3 5.0 F5 5.0 F5 5.0 F5 5.0 F5 5.0 F5 5.0 F5 5.0 F6 5.0 F6 5.0 F6 5.0 F7 F6 5.0 F7 F7 F6 5.0 F6 F7 F6	C8	10.0	50
C11 10.0 100 100 C12 10.0 100 CC (Control) 0.0 CC	C9	10.0	50
C12 10.0 100 CC (Control) 0.0 100 Russell Soil 50 R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	C10	10.0	100
Russell Soil 5.0 50 R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100			
Russell Soil R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	C12	10.0	— · ·
R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	CC (Control)	0.0	100
R1 5.0 50 R2 5.0 50 R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	Russell Soil		50
R3 5.0 100 R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100		5.0	50
R4 5.0 100 R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	R2		
R5 5.0 100 R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	R3		
R6 5.0 50 R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	R4	5.0	100
R7 10.0 50 R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100			
R8 10.0 50 R9 10.0 100 R10 10.0 100 R11 10.0 100	R6	5.0	50
R9 10.0 100 R10 10.0 100 R11 10.0 100			
R10 10.0 100 R11 10.0 100			
R11 10.0 100			
מום ומ			
	R12	10.0	100
RC (Control) 0.0	RC (Control)	0.0	

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- 2. 7:30 A.M.-4:00 P.M.: Conducted necessary analyses.
- 3. 4:00-7:00 P.M.: Prepared and attached sample bottles to columns. Added DI water to IV bottles and adjusted flow rates as needed.

The times indicated were the approximate times during which the tasks were begun and do not indicate the time necessary for completion of a particular task.

RESULTS AND DISCUSSION

The column studies discussed in Preliminary Investigations were operated continuously for 132 consecutive days. During this same time span, additional studies and tests were also conducted as part of the overall research program. studies included determination concurrent adsorption isotherms; elution of TCE from soil columns; effect of nutrient addition to the soil columns on the fate of TCE; TCE degradation studies; and analysis of from the test columns to determine the amount of TCE that remained at the end of the column studies. To achieve overall accounting for the TCE applied to each column, all results from the various means by which TCE was retained or eluted from the soil columns were pooled in a mass balance.

Batch Adsorption Studies

Soil Adsorption Isotherms

Equilibrium adsorption isotherms were determined for composite mixtures of each of the Chalmers and Russell soils. For each soil, the effect of particle size on adsorption was studied with soil mixtures of coarse particle size and fine particle size as discussed in Materials and

Methods. Experimental results used to determine the isotherms are listed in Table 23 and Table C1 of Appendix C. All adsorption isotherms were best described by the Freundlich theory as shown by Equation 3. The values of the Freundlich equation constants K_F and 1/n were determined from a least squares fit of the data in Table 23. The Freundlich constants are summarized in Table 24 based upon an equilibrium TCE concentration in mg/l and X/M expressed as ug of TCE adsorbed/g of soil.

Several observations can be drawn from the data of Table Since 1/n values were not equal to unity, adsorption 24. could not be considered linear over the range of TCE concentrations used to determine the isotherms. the 1/n values were close to unity and evaluation of the portrayed in Figures 9 and 10 indicated slight increase in adsorption at higher TCE equilibrium concentrations. There appeared to be no observable difference between the l/n values for coarse particle soil and fine particle soil. Rather, the differences in 1/n values for the different particle sizes of a particular soil were probably due to experimental error inherent in the analysis procedure and the method used to generate the isotherms. It did appear, however, that both particle sizes of Chalmers soil had 1/n values slightly greater than the corresponding 1/n values for each of the particle sizes of Russell soils. The difference, however, was not great and no significance should be attached to this difference.

Table 23. Summary of Experimental Values Used to Determine Soil Adsorption Isotherms for TCE.

C _i , mg/l	C _b , mg/l	% Loss	*C _e , mg/l	+X/M, ug/l
	Chalmers Sc	oil, coarse pa	article size	
110	85	22.7	64	42
220	167	24.0	130	73
440	354	19.5	273	164
660	493	25.3	349	294
880	717	18.5	564	307
1100	968	12.0	772	399
	Chalmers	Soil, fine pa	article size	
220	205	6.8	130	153
440	364	17.3	250	232
660	631	4.9	424	428
880	747	15.1	503	491
1100	987	10.3	627	727
	Russell S	oil, coarse p	particle size	<u>2</u>
110	90	18.2	74	33
220	175	20.5	159	32
440	371	15.7	331	81
660	491	25.6	429	125
880	720	18.2	631	182
1100	896	18.5	772	242
	Russell	Soil, fine pa	article size	
110	91	17.3	68	47
220	172	21.8	142	61
440	370	15.9	302	139
660	516	21.8	426	178
880	756	14.1	628	261
1100	920	16.4	701	442
				·

^{*} Average of two values. + Calculated from average values.

Table 24. Freundlich Constants Determined from Equilibrium Adsorption Isotherms for TCE Applied to Soils.

Parameter	Chalmers	Soil	Russell boil		
	Coarse	Fine	Coarse	Fine	
+K _F	0.813	1.250	0.443	0.826	
+1/n	0.949	0.972	0.926	0.910	
r ²	0.941	0.962	0.901	0.922	
% organic carbon	1.4	1.4	0.53	0.53	
*K _{OCF}	58.1	89.3	83.6	155.8	

^{*} Calculated from Eq. 6

Table 25. Calculated X/M Values for Various TCE Concentrations.

Soil Type	X/M (ug/g or X(g)) TCE E	quilibriu 500	m Conc.,	mg/l 1100**
Chalmers (coarse)	X/M	64	296	626	1,894
	X	0.346	1.599	3.381	10.229
Chalmers (fine)	X/M	110	525	1,130	1,894
	X	0.594	2.836	6.103	10.229
Russell	X/M	32	140	290	717
(coarse)	X	0.181	0.792	1.641	4.05
Russell	X/M	55	236	484	717
(fine)	X	0.311	1.336	2.739	4.05

^{*} Calculated from Freundlich isotherm constants.

⁺ Based upon TCE equilibrium concentration in mg/l and X/M in ug/g

^{**} Calculated from Karickhoff's relationship, Eq. 8

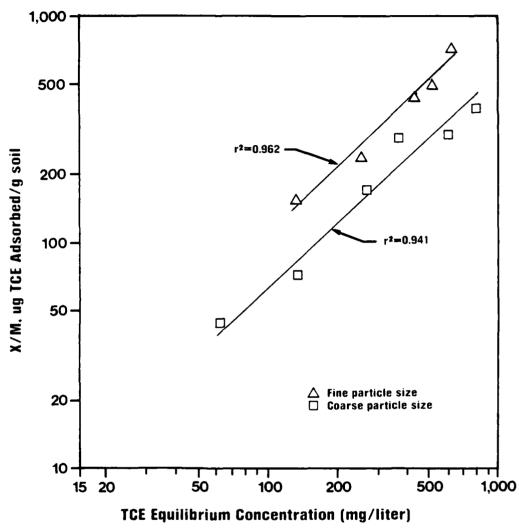


Figure 9. TCE Adsorption Isotherm for Composite Mixture of Chalmers Soil.

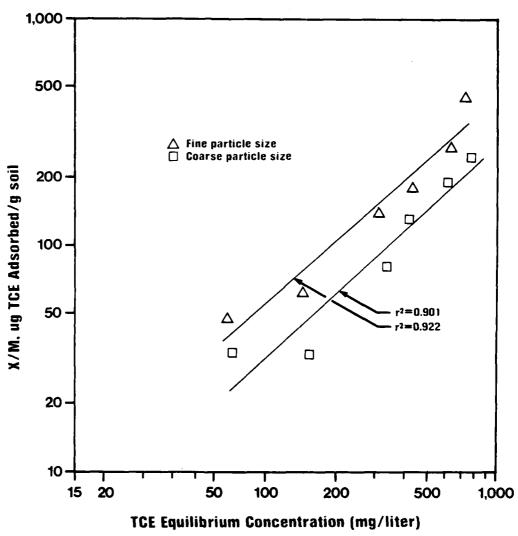


Figure 10. TCE Adsorption Isotherm for Composite Mixture of Russell Soil.

The values determined for $K_{\rm F}$ differed depending upon soil type and particle size. As shown in Table 24, for both particle sizes, the Chalmers soil exhibited higher K_F values than the Russell soil which had the lower organic carbon content of the two soils. Additionally, for both soils, the Kp determined on fine particle soil was greater than that determined for coarse particle soil. While the increase in Kr from coarse to fine particle size for Chalmers soil was only 52.6%, the increase for Russell soil was 86.5%. increase in Kp, with decrease in particle size, would seem to indicate that adsorption capacity depended upon surface Since both soils were composited, ground, and sieved area. in the same manner, it was unlikely that the different values for KF were due solely to difference in handling. Considering that Karickhoff (38) found that most organic carbon in soil is associated with the fine particles (<50 microns), grinding of the coarse particles into the smaller particles probably exposed very little additional organic surface area sites for adsorption. However, the same grinding could have exposed additional inorganic surface area adsorption sites thereby increasing Kr. The numerical increases in KF from coarse to fine particle size soil isotherms (0.437 for Chalmers and 0.383 for Russell) are comparable. Consequently, if all the organic carbon was in the fines fraction it would have passed through the No. 100 sieve even without grinding. Therefore, the grinding would

seem to have increased the inorganic surface area approximately equally for each soil.

A further indication of adsorption onto inorganic surface areas was shown by the K_{OC} 's calculated for the soils. If it is assumed that only organic carbon controls adsorption, the K_{OC} 's for each of the soils should have been reasonably similar. As shown in Table 24, however, the K_{OCF} 's differed. For the coarse particle sizes, the Russell K_{OCF} was 53.7% greater than that for Chalmers soil, while for the fine particle size, the Russell K_{OCF} was 86.4% greater. This comparison is important for it indicated that in this study organic carbon content alone did not solely control the adsorptive capacity of the soils tested.

Calculated values of adsorptive capacity based upon the Freundlich isotherms are shown in Table 25. As a comparison, X/M values calculated according to Karickhoff's relationship (38) of Equation 8 are also listed. It should be noted that the values calculated with a TCE concentration of 1,100 mg/l (maximum solubility of TCE) were extrapolated values since none of the isotherm tests used a TCE equilibrium concentration greater than 772 mg/l (Table 23).

Generally, Karickhoff's relationship (38) estimated X/M values 1.5 times higher than those predicted by the isotherms for the fine particle soil and 2.5-3.0 times higher than X/M values predicted by isotherms from coarse particle soil. While the difference was large, it must be

remembered that Karickhoff (38) expected his equation to have an accuracy only within a factor of two. Additionally, Equation 8 is a linear adsorption relationship based solely on organic carbon content with no consideration for inorganic surface adsorption and particle size effects. The isotherms determined in this study did account for particle size effects. As shown by the results of Table 24 and Figures 9 and 10, the particle size of the soil used to determine the isotherm had a measurable effect on the KF values.

Adsorption Equilibrium Study

As discussed in the Literature Review, various equilibrium times have been used for batch determination of soil adsorption isotherms. The equilibrium times used in this study were based upon the 18-hour times used by Richter (70) but lengthened to 48 hours. This increase was used because of the approximately 1,000 fold increase in initial TCE concentrations used.

After determination of the adsorption isotherms, it was desired to determine if equilibrium had, in fact, been reached during the 48 hour contact period. Consequently, a simple experiment was conducted to determine the time necessary for adsorption to reach equilibrium for both particle sizes of each soil type. A number of vials with soil were prepared for isotherm studies (as discussed in Materials and Methods) at TCE concentrations of 220 and 880

mg/1. These concentrations were chosen to represent the low and high TCE levels used in the isotherm determinations. An equal number of blanks were prepared that corresponded to the number of soil adsorption vials. All vials were incubated on an operating shaker table at 20°C. Approximately ten times per day all vials were inverted to maximize mixing. At intervals during the 48 hours, one adsorption vial and one corresponding blank were removed and analyzed for TCE solution concentration as discussed in Materials and Methods. The results of this experiment are shown in Tables 26 and 27 with liquid volumes and soil masses used shown in Table C2 of Appendix C.

The degree of attainment of equilibrium was based on the ratio of X/M determined from the time of adsorption experiment to X/M calculated from the appropriate adsorption isotherm for the C_e value determined for the particular time of adsorption. With this procedure, if the ratio was less than 1.0, then maximum adsorption had not been achieved up to that particular time. An assumption made in using this approach was that equilibrium would, in fact, be attained during the 48-hour contact period. This assumption proved correct as shown by the X/M ratios listed in Tables 26 and 27 and graphically illustrated in Figures 11,12,13, and 14.

In all cases, equilibrium appeared to have been reached after 20 hours of agitating and mixing the adsorbent (soil) and adsorbate (TCE in solution). More specifically, the

Data from Time of Adsorption Experiment for Chalmers Soil Subjected to TCE Application. Table 26.

Coarse particle		& Loss	ce, mg/l	(X/M)t, ug/g	'(X/M) _i , X/M ratio ug/g (X/M) _t /(X/M) _i	<pre>(/M ratio /M)t/(X/M);</pre>
c	article size,	$c_i = 220 \text{ mg/l.}$				
Ŋ	184	16.4	7	18	109	
4	173	21.4	165	16	103	0.15
9	186	15.5	9	47	102	4
J)	169	23.2	3	62	87	7
13	174	20.9	3	9/	98	œ
23	172	21.8	\sim	79	84	9
33	183	16.8	~	73	80	9
48	173	21.4	\sim	81	82	9
Coarse p	particle size,	$C_{i} = 880 \text{ mg/l}.$				
7	744	•	N	46	419	_
4	749	14.9	721	57	419	0.14
•	737		2	162	383	4
эл	721		_	225	357	9
13	703		9	293	330	8
23	729		7	314	337	9
33	758		9	338	347	6

Table 26. Continued.

C

Time, hours	Cb, mg/l	% Loss	C _e , mg/l	*(X/M) _t , ug/g	+(X/M); X ug/g (X/	X/M ratio (X/M) _t /(X/M) _i
Fine particle	size, C _i =	220 mg/l.				
7	2	•	9	49	182	.2
4	σ	•	5	95	165	3
9	9	3,	4	66	153	9.
9.5	188	14.5	~	128	139	9
13	∞	9	~	125	132	6.
16	æ	4.	7	132	135	6
24	∞	5.	_	137	129	0
36	∞	5.	2	134	134	6
48	7	0	116	121	127	
Fine particle	size, C _i =	880 mg/l.				
2	9	2	691	157	719	.2
4	757	14.0	809	303	635	0.48
9	4	5.	573	364	009	•
9.5	Ø	•	542	493	568	ω.
13	5	4.	501	515	526	6.
16	S	4.	489	529	514	0
24	9	3.	496	545	521	0.
36	3	4.	479	548	504	0
84	9	.	507	517	532	6.

from time of adsorption experiment. from isotherm for Ce value listed. = X/M value determined = X/M value calculated value calculated $(X/M)_t$ + $(X/M)_i$

Data from Time of Adsorption Experiment for Russell Soil Subjected to TCE Application. Table 27.

Specification of the second second

				•		
Time, hours	Cb, mg/1	& Loss	Ce, mg/l	*(X/M)t, ug/g	+(X/M); ug/g	⁺ (X/M) _i , X/M ratio ug/g (X/M) _t /(X/M) _i
Coarse p	particle size,	$C_{i} = 220 \text{ mg/l.}$				
2	181	7.	7	œ	53	•
4	173	ï.	9	14	20	•
9	174	0	9	24	49	•
6	177	19.5		22	20	0.44
	169	ω,	5	36	46	•
18	182	7.	5	26	47	•
24	173	i.	4	48	46	•
38	170	2	4	46	45	
48	176	0.	150	51	46	1.11
Coarse p	particle size,	$C_i = 880 \text{ mg/l}.$				
7	4	5.	727	30	6	7
4	3	9	718	36	6	7
9	4	5.	200	88	9	4
S	\sim	7.	899	~	∞	9
14	3	7.	638	7	7	0
18	3	9	643	ω	7	0
24	707	19.6	618	179	170	1.05
38	7	α	622	œ	~	0
48	S	7.	630	9	7	٦.

Table 27. Continued.

Time, hours	Cb, mg/l	& Loss	Ce, mg/l	*(X/M)t, ug/g	+(X/M);, ug/g	+(X/M) _i , X/M ratio ug/g (X/M) _t /(X/M) _i
Fine particle	size, C	$i_1 = 220 \text{ mg/l}.$				
7	7	19.1	7	16	88	0.18
4	174	20.9	161	26	84	0.31
9	7	20.0	S	48	80	0.60
	7	21.8	4	99	74	0.89
	œ	18.2	4	72	92	0.95
24	7	20.0	3	74	74	1.00
	7	22.7	3	73	71	1.03
	9	23.2	3	69	72	96.0
	7	18.6	4	79	75	1.05
Fine particle	icle size, C	i = 880 mg/l.				
7		3	723	70	330	0.21
4	740	15.9	702	78	321	0.24
9		•	693	219	318	9
		•	644	232	297	7
		4.	626	273	290	9
		٠;	638	289	295	9
33		•	619	293	287	0
		5.	809	269	282	9
		į.	636	290	294	9

 $^*(X/M)_t = X/M$ value determined from time of adsorption experiment. $^*(X/M)_1 = X/M$ value calculated from isotherm for C_e value listed.

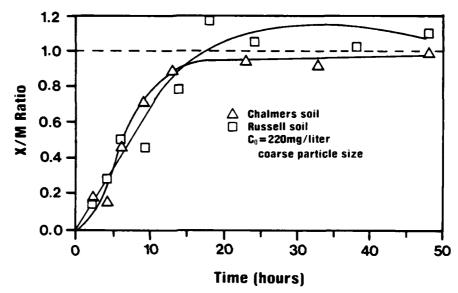


Figure 11. Adsorption Equilibration for Coarse Particle Soil with TCE Concentration of 220 mg/l.

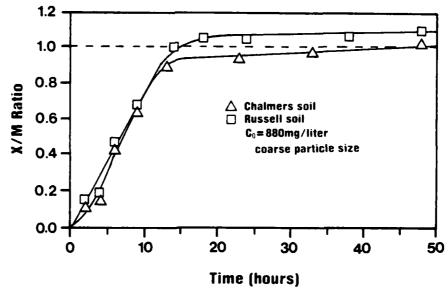


Figure 12. Adsorption Equilibration for Coarse Particle Soil with TCE Concentration of 880 mg/l.

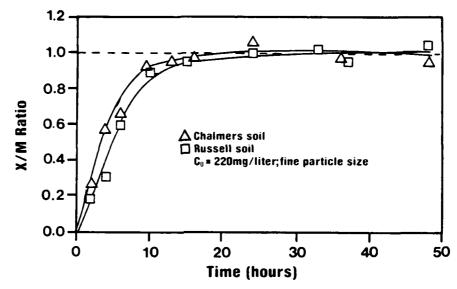


Figure 13. Adsorption Equilibration for Fine Particle Soil with TCE Concentration of 220 mg/l.

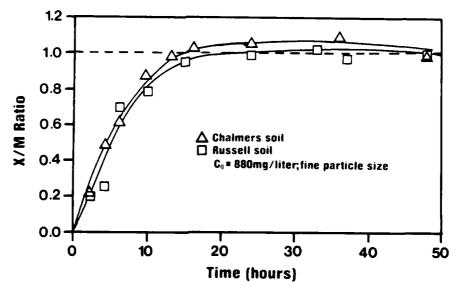


Figure 14. Adsorption Equilibration for Fine Particle Soil with TCE Concentration of 880 mg/l.

fine particle soil reached equilibrium by 15 hours. This slightly faster approach to equilibrium by fine particle soil was not unexpected since the smaller particle size can allow more rapid diffusion into the pores of the adsorbent (98). As shown in Figures 11-14, there appeared to be little difference between the Chalmers and Russell soils in the attainment of equilibrium for both particle sizes and TCE concentrations studied. Except for the combination of coarse particle size and 880 mg/l TCE concentration, the Chalmers soil appeared to approach equilibrium more rapidly. For the combination of coarse particle size and 880 mg/l TCE concentration, the Russell soil appeared to approach equilibrium more rapidly.

This experiment indicated that maximum adsorption by the soils occurred by at least 20 hours. Consequently, the 48-hour contact period was sufficient to allow the adsorbents and adsorbates to reach equilibrium, therefore establishing the validity of the isotherms.

Adsorption by Glass and Gravel

Within the soil columns, the glass surface of the tubing and the gravel at the bottom of the column were also possible adsorbents for TCE during the studies. To assess the adsorptive capacity of glass and gravel, separate adsorptive studies were conducted according to procedures described in Materials and Methods. The results of these studies are shown in Tables 28 and 29 with liquid volumes

Table 28. Summary of Data from Glass Adsorption Study with TCE.

C_i , mg/l	C _b , mg/l	% Loss	C _e , mg/l	X/M, ug/g	*X/A, ug/cm ²
220	196	10.9	191	8.0	1.20
440	401	8.9	398	5.0	0.73
660	572	13.3	580	-13.2	-1.91
880	743	15.6	756	-21.4	-3.12
1100	894	18.7	893	1.6	0.24

^{*} X/A = ug TCE adsorbed/cm² of glass surface area (Calculated in Appendix C)

Table 29. Summary of Data from Gravel Adsorption Study with TCE.

C_i , mg/l	C _b , mg/l	% Loss	$^{\mathrm{C}_{\mathbf{e}}}$, mg/l	X/M, ug/g
110	89	19.1	88	2
220	187	15.0	193	-12
440	372	15.5	369	5
550	479	12.9	481	-4
660	593	10.2	586	12
880	774	12.0	772	3
1100	939	14.6	935	7

and adsorbent masses used in the experiments listed in Tables C3 and C4 of Appendix C.

For both gravel and glass, adsorption appeared to be minimal, erratic, and not to fit any standard isotherm relationship. In fact, several "negative" X/M values were obtained, presumably due to a higher volatile loss from the blanks than adsorption plus volatile loss from adsorption bottles. Because of the randomness of the data, no plots to establish isotherms were made. It was apparent, though, that the glass and gravel provided negligible adsorption compared to soil.

The gravel surfaces, for all practical purposes, could be considered inorganic. Additionally, the surface area per unit weight of the 1/4"-3/8" gravel was exceedingly small, on weight basis, compared to that of the soil particles. The largest X/M value found in Table 29 was 12 ug/g. When this value was used to determine the adsorptive capacity of 369 g of gravel (the average amount of grivel in the 2-inch deep column well), it indicated only 4.428 mg of TCE could have been adsorbed by the gravel. For this reason, TCE adsorption by the gravel was neglected at the TCE concentrations exhibited during the course of this study.

Similarly, the glass surfaces of the column were also inorganic with 2,234 $\rm cm^2$ of glass area exposed to TCE solution on the interior of the glass tubing. Since, from Table 28, the largest X/A (ug TCE adsorbed/cm² of glass

surface area) was 1.20, the maximum amount of TCE adsorbed by the glass could have been 2.6 mg. Because this calculated amount was small, TCE adsorption by glass was neglected.

Other small amounts of the TCE could have possibly been adsorbed by the effluent needle, collector tube, and rubber collar shown in Figure 3. While not quantitatively determined during the study, TCE adsorption by these items was neglected due to their exceedingly small surface contact area and based upon results of the gravel and glass adsorption tests. Consequently, adsorption by materials other than the soil of the column was considered negligible and was not accounted for during the course of the column studies.

Volatilization Losses

One problem associated with working with volatile compounds such as TCE is their disappearance from solution via volatilization. Richter (70) and Rogers et al. (75) reported volatilization losses in their studies but did not analytically quantify the losses. As indicated by Tables 23,26,27 and 28, all blank adsorption vials used for the various experiments of this study showed loss of TCE. There appeared to be no particular pattern to the percentage of TCE lost from the adsorption blanks based upon initial TCE concentration, soil type, or particle size. Additionally, there appeared to be no major difference in percentage lost

between the 25 ml soil adsorption vials (which used screw caps and septa) and the 125 ml serum bottles (which used crimp caps and septa) used for glass and gravel adsorption.

The time of adsorption study (Tables 26 and 27) did not generally indicate an increased volatilization loss with increased time of equilibrium. Rather, the loss appeared to be randomly distributed throughout the sampling periods, and largely, within a range of 10-20% of the amount of TCE These facts seemed to indicate that loss of TCE present. while determining adsorption isotherms occurred during sample preparation and retrieval rather than during sample equilibrium. Since the adsorption blanks were treated exactly as adsorption vials, differences in volatilization losses due to handling were minimized. Additionally, since the soils used in these batch adsorption studies were sterilized, the loss of TCE from solution in the adsorption vials was solely due to volatilization and adsorption and not biological degradation. Since volatilization accounted for with the blanks, adsorption was determined in a valid manner.

Column Elution Studies

General

The column elution studies comprised the bulk of the research effort of this investigation. Twenty-four hours after the TCE was applied to the soil columns, water was

applied for 132 consecutive days at the rates shown in Table 22. The purpose in applying the water was to determine the amount and pattern of TCE that could be eluted from the soil. The elution patterns were determined for the effluent TCE concentrations which were measured on each column effluent two to four times per week. Prior to discussion of effluent TCE concentrations, however, it is necessary to enumerate several methodology problems that arose early in the studies.

Daily effluent volumes collected were quite erratic during the early days of the investigation as shown by the daily data listed in Tables B2-B11 of Appendix B. A summary of the data for each column is listed in Tables 30 and 31. The initial erratic effluent volumes were caused by two factors. Occasionally, various effluent needles became obstructed or clogged from bits of septum which were gouged from the sample collection bottles. This was only a minor problem which was corrected by Day 20, but it prompted a routine check of each needle for bits of septum to prevent further problems.

The major cause of erratic water application rates was the problems associated with the IV tubing and screw clamps used to control the water flow from the IV reservoir to the delivery needle at the top of the column. As described in Preliminary Investigations, the IV bottle was to be filled with DI water which would slowly drip onto the column at the

Mean, Standard Deviation, and Range of Daily Volume of Effluent Collected from Chalmers Soil Columns. Table 30.

Residentation of the second of

Table 30. Continued.

	SD Range	Day 56 - Day 132	4.29 81-106	4.26 87-107	3,36 93-109	1	3.63 92-107	4.70 81-108	5.19 80-112
	Mean	Day	0.66	99.1	100.1	ı	99.3	7.66	99.5
ted, ml	Range	132	0-147	0.142	0-175 100.1	ı	0-138	0-139	0-144
Daily Volume of Effluent Collected, ml	SD	Day 0 - Day 132	16.19	15.26	18.87	1	16.34	16.91	16,52
Effluen	Mean	рау	98.3	7.76	6.86	1	97.0	8.86	101.2
lume of	Range	55	0-147	0-142	0-175	0-136	0-138	0-139	0-144 101.2
Daily Vo	SD	0 - Day 55	24.50	23.09	29.04	27.08	24.74	25.75	24.79
	Mean	рау 0	7.76	8.36	97.3	7.66	93.9	0.66	103.5
Column	1		C4	C 5	90	C102	C11	C12	Control 103.5

Note: 1. C7 removed on Day 121 2. C10 removed on Day 44

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Table 31.		ean, olle	Standarc cted from	d Deviat n Russel	tion, an 11 Soil	d Range c Columns.	of Daily	Volume	Mean, Standard Deviation, and Range of Daily Volume of Effluent Collected from Russell Soil Columns.	nt
Column			Dã	ily Vo	lume of	Daily Volume of Effluent Collected , ml	Collect	ed, ml		
	Mean		SD	Range Mean	Mean	SD	Range	Mean	SD	Range
		Бау	Day 0 - Day 70	070	Бау	Day 0 - Day 132	132	Day	Day 71 - Day 132	132
Rl	54.3		15.74	0-101	52.3	11.73	0-101	50.1	2.41	45-53
R2	55.5	١٥	14.25	0-84	52.7	10.89	0-84	49.5	2.19	45-54
R3	54.8	m	15.52	0-75	53.6	13.71	0-75	50.0	3.07	39-61
R71	51.6	م	22.10	06-0	i	ı	1	1	1	ı
ж 8	53.0	0	13.71	0-91	51.6	10.20	0-91	50.0	2.52	44-54
R9	54.9	on.	15.73	0-87	52.7	11.76	0-87	50.2	2.19	46-54

Table 31. Continued.

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Column			Daily	Volume	Daily Volume of Effluent Collected , ml	ıt Coll	ected,	ml	
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
	Day 0	- Day 55		Дау 0	Day 0 - Day 132		Day 5	Day 56 - Day 132	32
R4	99.2	22.99	0-143	99.5	15.01	0-143	7.66	3,53	94-106
R5	94.7	23.66	0-139	9.76	15.66	0-139	8.66	3.82	93-109
к6	91.1	20.07	0-130	96.1	13.95	0-130	9.66	4.28	92-117
R10	99.4	24.65	0-137	6.66	16.14	0-137	100.2	4.15	88-106
R11	98.1	22.12	0-142	8.86	14.48	0-142	99.3	3.61	88-109
R122	6.96	24.33	0-132	ı	1	Į,	1	1	ı
Control 103.5	103.5	24.79	0-144 101.2	101.2	16.52	0-144	99.5	5.19	80-112

Note: 1. R7 removed on Day 44.

prescribed rate until the IV bottle needed be During column setup in preliminary experiments, refilled. all delivery systems were calibrated for the proper rates. Once the studies began, daily adjustments in flow rates were Eventually, these adjustments began to restrict the made. tubing and to produce permanent crimps which severely restricted the flow. Efforts to relieve the crimps and errors in adjusting the screw clamps allowed some excessive water applications. Consequently, to reduce the excessive amount of time spent adjusting the tubing, a different application method was instituted on Day 40.

The new method, similar to that used by Emig (22) and Wentink (100), consisted of placing the daily volume of DI water into the appropriate IV bottles on a daily basis. This volume was then allowed to drip onto the columns at a controlled rate. In most cases, the volume of water was applied to the column over a 10-12 hour period.

This method vastly improved the delivery rate as evidenced by the data on effluent volumes in Tables 30 and 31. These tables show the mean, standard deviation, and range for effluent volumes for the initial stage, latter stage, and complete duration of the study. The division between the initial stage and latter stage was determined from a residence time estimated from the application rate and the calculated pore volume of the columns. The calculated pore volume of the Chalmers column was 1,706 ml

while that for the Russell column was 1,617 ml. 50 ml/day application rate, the calculated residence time for the Chalmers column was 34.1 days and 32.3 days for the Russell column. Since, as discussed in Literature Review, the actual residence time would be less than that calculated, 30 days was used as an estimate of residence time for both soil columns for 50 ml/day. Similarly, for 100 ml/day, 15 days was used as an estimate for residence time for both soil columns. The initial stage listed in Tables 30 and 31 encompasses the time period up to the change in application method (Day 40) plus one residence time (15 or 30 days).

As shown in Tables 30 and 31, control of the flow rate improved over the latter stage of the study as compared to the initial stage. Evidence to this are mean values of flow rates that are closer to the desired flow rates, smaller standard deviations, and smaller ranges of flow rates. While overall in the initial stage the mean values of effluent volumes were close to the desired rate, there were wide fluctuations as shown by the wide range and high standard deviations. Some flow variations did exist in the latter stage, however, most of this was accounted for by the one to four hour variation in time on a daily basis in which samples were collected or delivery bottles replenished.

It was initially planned to periodically sacrifice or take apart selected columns during the study to determine

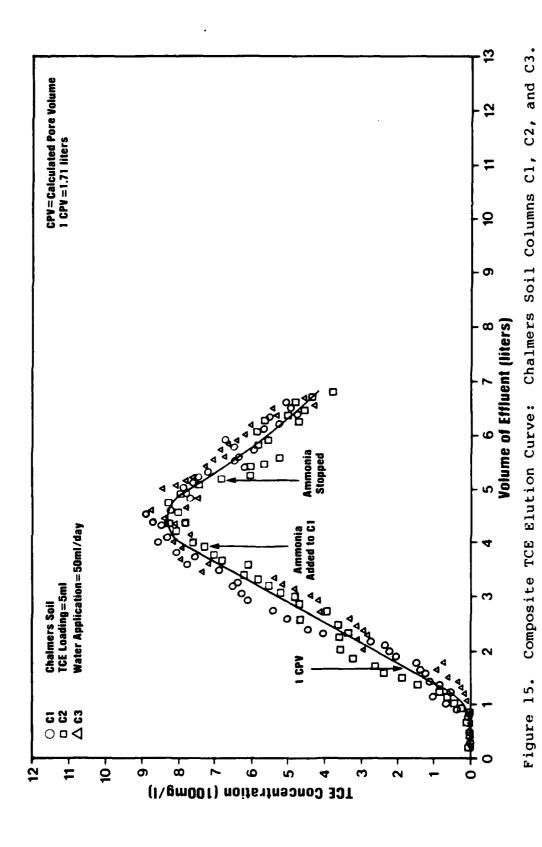
the location and magnitude of TCE movement through the soil. However, the glass tubing of columns C10 and R12 were found broken on Days 44 and 45, respectively. Since the breaks were located at the bottom of the column, it was speculated that the weight of the soil column caused the bottom stopper to act like a wedge and to fracture the glass. Regardless of the cause, the idea of periodically sacrificing columns was discarded to prevent unnecessary reduction in the triplicate columns in each column grouping.

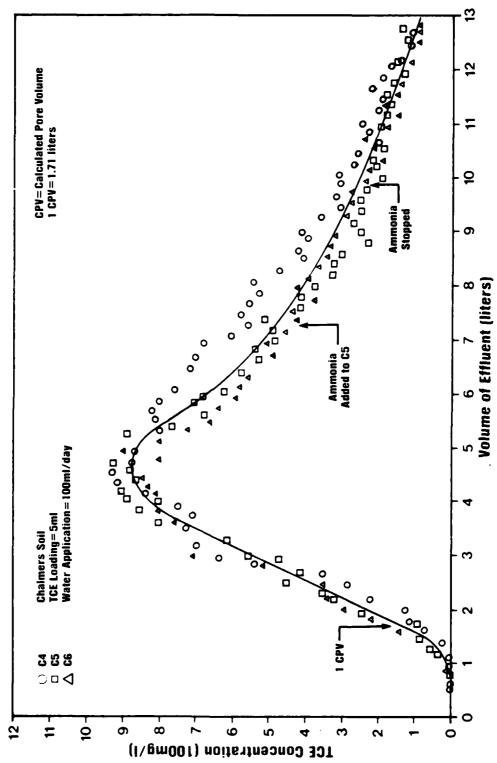
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TCE Elution

To graphically illustrate the TCE elution patterns for the different soils, water application rates, and TCE mass loadings, the TCE concentrations listed in the daily data of Appendix B were plotted for each specific test column loading and operating condition. These plots, using effluent volume as the common basis of comparison, are shown in Figures 15-22. In the figures, a composite elution curve was drawn through all data points for the specific column tests. This approach was used because on a day to day basis the cumulative effluent volumes differed and never matched well enough to allow for calculation of a mean value.

As anticipated, the use of triplicate columns allowed the fluctuation of any particular column to be compensated for by the response of similar columns. This was evident in all of the composite elution curves of Figures 15-22. For

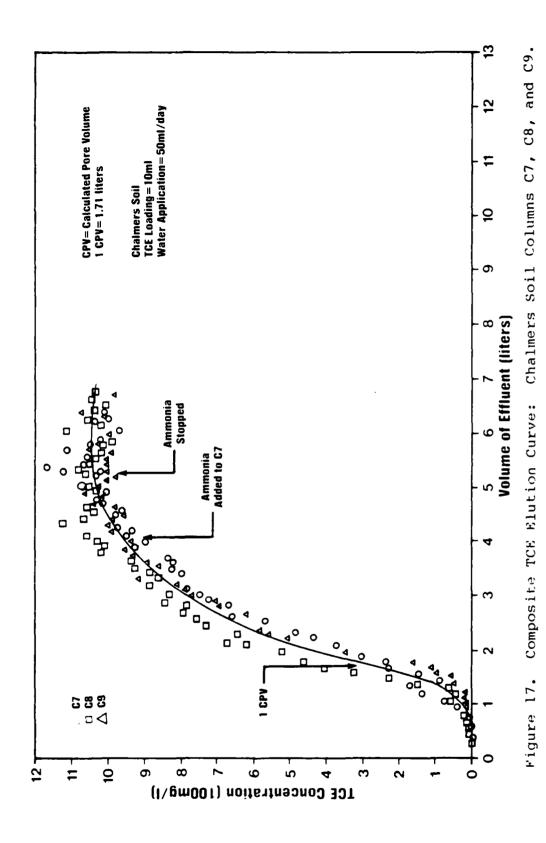




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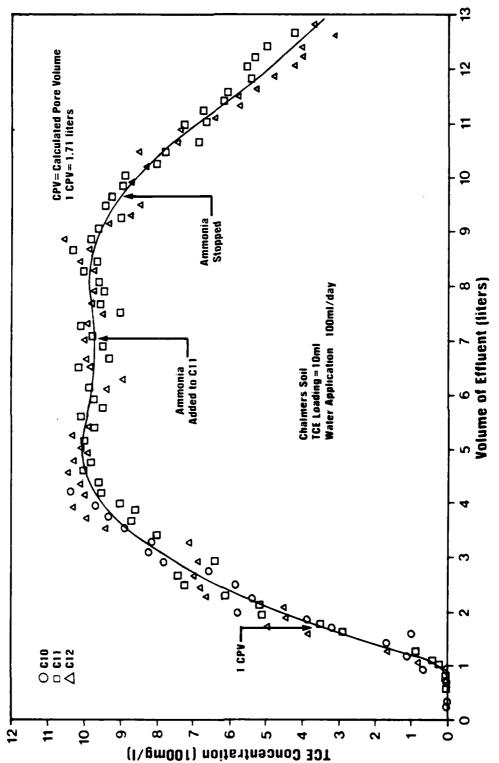
Chalmers Soil Columns C4, C5, and C6. Composite TCE Elution Curve: Figure 16.



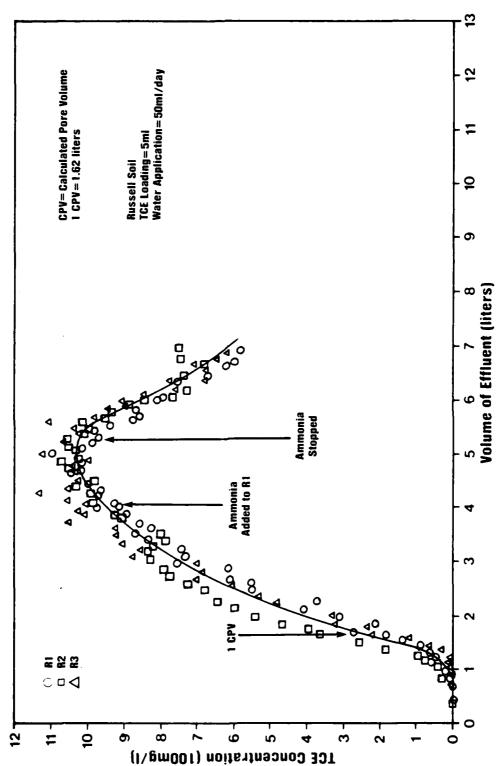
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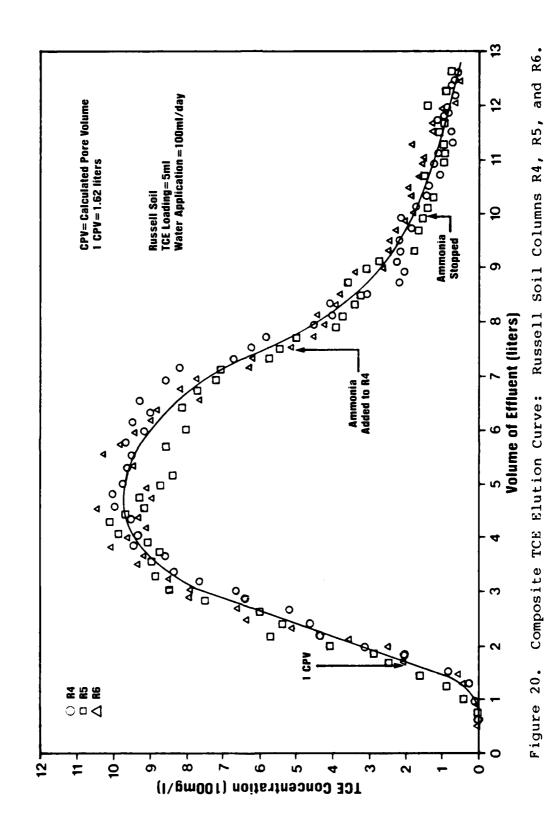
Chalmers Soil Columns Cl0, Cl1, and Cl2. Composite TCE Elution Curve: Figure 18.

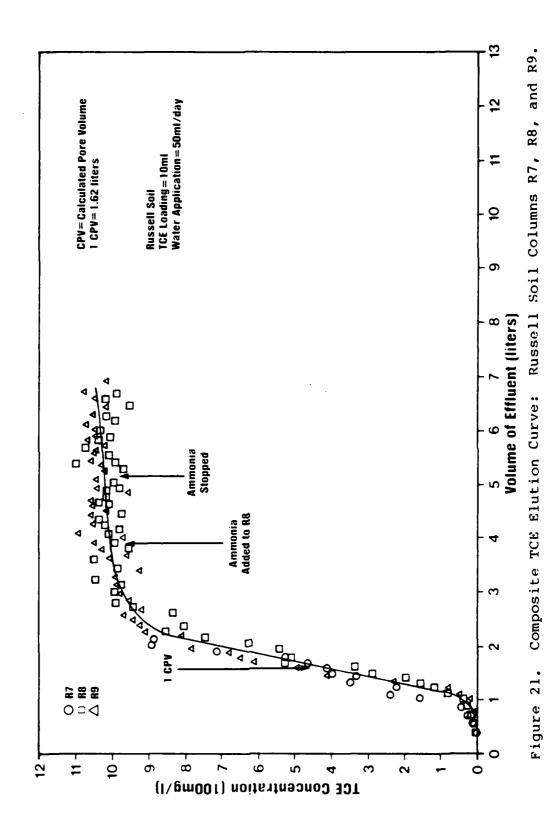


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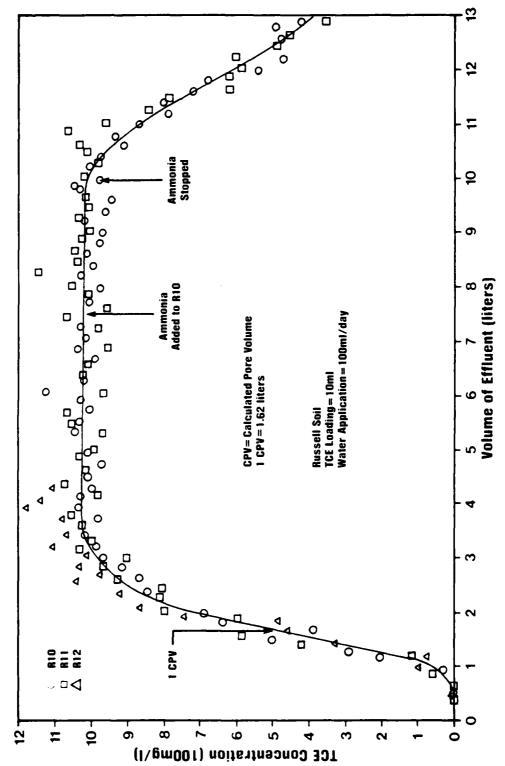
Russell Soil Columns R1, R2, and R3. Composite TCE Flution Curve: Figure 19.





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Composite TCE Elution Curve: Russell Soil Columns R10, R11, and R12. Figure 22.

each specific column test, the composite plot allowed a smooth curve to be drawn. On the other hand, if one followed the periodic fluctuations of TCE concentrations for any one specific column, the TCE elution pattern may be somewhat different from the composite elution patterns. Before comparing the composite elution curves on the basis of organic carbon, TCE loading, and water application rate, the elution curve for each specific column test group (identified in Table 22) will be discussed separately.

Columns C1-C3 (Figure 15, Table B2). TCE was initially detected in these effluents at 0.18 Calculated Pore Volumes (CPV) of cumulative effluent. Concentrations gradually increased to the mg/l range by 0.5 CPV. At 1.0 CPV, the composite elution curve indicated an effluent concentration of approximately 220 mg/l. From an effluent volume of approximately 1.3 l to 4.0 l, the TCE concentration increased to approximately 810 mg/l in an apparent linear manner. From 810 mg/l, the concentration gradually increased to a maximum of 840 mg/l at 4.5 l. Beyond this, there was a gradual, then almost linear, decrease in TCE concentration. The elution curve was slightly asymmetrical and exhibited some tailing on the descending portion.

Columns C4-C6 (Figure 16, Table B3). TCE was initially detected at 0.23 CPV. Concentrations in the mg/l range appeared by 0.47 CPV with a TCE concentration of 140 mg/l at 1.0 CPV on the composite elution curve. This concentration

increased linearly to 820 mg/l at 4.0 l of effluent volume then to a maximum of 880 mg/l. The TCE concentration then declined in a linear fashion for approximately 0.5 l, at which point the rate changed from linear to a decreasing rate of decrease. The elution curve was asymmetrical and exhibited tailing on its descending concentration portion. Columns C7-C9 (Figure 17, Table B4). By 0.16 CPV, TCE was detected in the effluents with mg/l concentrations by 0.27 CPV. At 1.0 CPV the TCE concentration was 320 mg/l on the composite elution curve. Concentrations on the composite curve reached a maximum of 1,050 mg/1 at 5.25 l and stayed constant through the final effluent value of 6.7 1. the final concentration did not decrease from the maximum, it could not be determined whether the elution curve was symmetrical or asymmetrical. Column C7 was removed from service on Day 122 when the bottom of the glass tubing was found to be broken.

Columns C10-C12 (Figure 18, Table B5). TCE was initially detected at 0.19 CPV and by 0.43 CPV had reached the mg/l concentration. By 1.0 CPV on the composite elution curve, the concentration was 365 mg/l. The concentration increased at a decreasing rate to 1,020 mg/l on the composite curve, slightly decreased to 980 mg/l then increased to 1,000 mg/l. At this point the TCE began to decrease until the final concentration was 340 mg/l at 13 l final volume. The elution curve was asymmetrical and exhibited slight tailing

toward the final stages of elution. As discussed previously, column ClO was removed from service on Day 44 because of a break in the glass tubing.

Columns R1-R3 (Figure 19, Table B7). TCE was initially detected at 0.25 CPV with concentrations in the mg/l range by 0.43 CPV. By 1.0 CPV on the composite elution curve, the concentration had reached 280 mg/l and climbed to a maximum of 1,050 mg/l at 5.0 l cumulative effluent volume. From this point, the TCE concentration decreased to 655 mg/l at the final effluent volume of 7.0 l. No tailing was noted; however, the elution curve appeared to be slightly asymmetrical.

Columns R4-R6 (Figure 20, Table B8). Initial detection of TCE came at 0.32 CPV. By 1.0 CPV the composite elution curve indicated a concentration of 200 mg/l. This concentration increased linearly to a broad peak with a maximum concentration of 980 mg/l. This broad peak initially decreased at an increasing rate until approximately 3.0 l of effluent volume. At this point, the rate of decrease slowed until the concentration was 40 mg/l at the final effluent volume of 12.7 l. This elution curve was asymmetrical with extensive tailing compared to the other column elution patterns.

Columns R7-R9 (Figure 21, Table B9). TCE was initially detected at 0.17 CPV with mg/l concentrations appearing by 0.38 CPV. By 1.0 CPV the concentration on the composite

elution curve was 440 mg/l. Beginning at approximately 1.0 l effluent volume (0.62 CPV), the TCE concentration increased linearly to 850 mg/l then tapered off to a maximum of 1,040 mg/l at the final effluent volume of 7.0 l. Since the concentration had not begun to decrease by the end of the investigation, it could not be determined if the elution curve would exhibit tailing or asymmetry. Column R7 was removed from service on Day 45 due to the appearance of free or undissolved TCE in the sample collection bottle as discussed later in this section of the thesis.

Columns R10-R12 (Figure 22, Table B10). TCE was detected by 0.25 CPV with mg/l levels by 0.30 CPV which showed a rapid increase by 0.65 CPV. At 1.0 CPV, the TCE concentration on the composite elution curve was 480 mg/l. The concentration increased to a maximum of 1,040 mg/l at 3.4 l then stayed constant until approximately 10 l of effluent volume. At this point the TCE concentration rapidly decreased in an apparently linear fashion. While no tailing was exhibited, the curve appeared to be asymmetrical. On Day 45 Column R12 was removed from service because of a break in the glass tubing.

General Information On All Columns. The erratic water application rate during the initial 40 days of the study presented two problems to all the column groups. One problem was that preliminary investigations determined the maximum water application rate for the soils to be 125 ml/

day. Although several daily applications exceeded this, no ponding was ever noted on the top of any columns. Another problem involved small effluent volumes collected for analysis. To ensure accuracy, 15 ml was the minimum effluent volume used for analysis. Consequently, during the initial 40 days of study, several small samples were not analyzed. Their volume, however, was logged into the daily cumulative effluent volume. This lack of data was most apparent in columns with the 100 ml/day water application rate.

None of the samples from the control columns indicated any detectable TCE in the effluent. This was expected because there was no history of any TCE spill or application on the site from which the soil cores were obtained. These negative results also indicated glassware was adequately cleaned. Since no blanks showed any detectable levels of TCE, the syringe cleaning procedures and quality of DI water used for dilution were also adequate.

At least one suspended solids analysis was run on each column during the period of Day 12 through Day 30. Since all results were less than 1.0 mg/l, there was no concern over a solids mediated effect on the head space analysis procedure. No further solids analyses were conducted. The clarity of the effluent was visually inspected daily; however, no turbid effluents were noted.

all columns, TCE was detected at various levels before 1.0 CPV of effluent had passed through the soil column. There were several reasons for this occurrence with one of the most obvious being short-circuiting between the soil core and glass tubing of the column. It appeared, free or undissolved TCE initially that no short-circuited the entire length of the column because the early phases of elution show no immediate increase before 1.0 CPV. Since TCE is more dense than water, free TCE could have traveled faster than water before adsorbing onto soil or dissolving in the water, thus advancing the concentration Another reason for the early appearance of TCE was that the soil was not a homogeneous medium but contained tortuous passageways. Some fractions of the effluent may have traveled shorter passageways than other fractions and exited before than 1.0 CPV. Additionally, since the pore volumes were not quantitatively measured, they could have actually been less than that calculated because of immobile regions of the pore volume (74). Since the pore volume was used only as a basis for comparison, the CPV was accepted as a valid parameter.

Only one column, R7, showed evidence of free or undissolved TCE in the effluent. On Day 44 several globules of liquid, a total estimated less than 0.1 ml, were noticed in the bottom of the sample collection bottle. After 1:1 and 4:1 dilutions with DI water, the headspace analysis

still showed TCE concentration at or over the maximum solubility of 1,100 mg/l. Subsequent to the dilution, 10 ml of methanol were added to the serum bottle and shaken. After this, the globules were no longer evident, indicating they were free TCE. In view of this finding, Column R7 was removed from service.

columns also showed effluent concentrations Other slightly greater than the maximum solubility of 1,100 mg/l. Figures 17,19,21, and 22 show those columns were C7,C8, R3, With only one dilution (as discussed in and R7-12. Materials and Methods), though, the highest concentration found was 1,193 mg/l. In this sample, as well as all others initially determined to be over 1,100 mg/l, subsequent dilution lowered the concentration in proportion to the dilution ratio. Additionally, no globules of TCE were visually noted in any sample bottle before or after Consequently, the dilution method used to dilution. maintain linearity also served as a check on the presence of free or undissolved TCE. The TCE concentrations over 1,100 mg/l may have been due to additive errors in determining sample volume, dilution water volume, and sample injection volume. Conversely, for the same reasons, some concentrations were probably calculated to be less than actual as evidenced by the fluctuation of concentrations on a day-to-day basis. This was especially evident for those columns charged with 10 ml of TCE.

Concern developed over the constant high concentrations of TCE in several of the column effluents. considered possible that these saturated or nearly saturated TCE concentrations could have been due to free TCE which migrated through the soil and coated the gravel or stayed as a pool on the bottom stopper. To check this possible cause, the gravel and stopper assemblies were removed and replaced with new gravel and stopper assemblies for the following columns on the indicated days and cumulative effluent volumes: C7, Day 80, 4.363 1; C8, Day 80, 4.208 1; C11, Day 55, 5.165 1; C12, Day 55, 5.446 1; R8, Day 78, 4.111 1; R9, Day 78, 4.240 1; R10, Day 78, 7.790 1; R11, Day 78 7.655 1. All of these columns had been loaded with 10 ml TCE. shown in Figures 17,18,21, and 22, changing the gravel and no effect stopper assemblies had the effluent concentrations. This reinforced the finding that, except for column R7, no free TCE was transported through the soil columns during the course of the investigation. saturated or nearly saturated effluent concentrations observed were consequently considered to be due to the TCE present in the soil.

Time of Saturation Study. As indicated in the discussion of specific column groups and as shown in Figures 15-22 and Tables B2-B11, TCE concentrations from some, but not all columns approached or exceeded 1,100 mg/l, the maximum solubility of TCE in water (45,51). The question arose as

to whether this finding was relevant in adsorption:desorption phenomena or whether it simply pertained to the time required for TCE dissolution. To answer this question, an experiment was conducted to determine the time required for a given volume of water to become saturated with TCE when TCE was present in excess of its maximum solubility.

The experiment was conducted as follows:

- 1. A number of 125 ml serum bottles were completely filled with DI water. Two ml (approximately 2.9 g) of TCE were pipetted into the mouth of the bottle so that the TCE settled through the water the entire depth of the bottle and the water displaced was allowed to overflow. The bottles were sealed with Teflon® faced septa and aluminum crimp caps and inverted three times to provide mixing. The bottles were allowed to remain quiescent at 20°C.
- 2. Periodically, one of the bottles was removed.

 A sample of TCE solution was withdrawn via a syringe needle through the septum with the end of the needle approximately mid-depth of the bottle.
- 3. The TCE concentration of the sample was determined according to the procedure listed in Materials and Methods.

Results of TCE concentrations determined during the study are listed in Table Bl2 of Appendix B and plotted in

Figure 23. As shown from the figure, the TCE concentration reached 90% of maximum by 25 hours, 95% by 30 hours, and 100% by 45 hours. This experiment was solely intended to indicate the magnitude of time required for maximum TCE dissolution. It was not intended as an accurate measure of dissolution kinetics.

Since the dissolution experiment was conducted with quiescent conditions, one must consider how this would compare to conditions within the soil column. Water was applied to the column drop-by-drop, so some mixing occurred at the point of soil:water contact. Since the pore volume of the soil contains a degree of tortuousity, additional mixing and contact was assured between the water and any adsorbed or free TCE. It was assumed that this degree of mixing would allow faster TCE dissolution than quiescent conditions would allow. Consequently, TCE dissolution within the soil column probably proceeded at a faster rate than that indicated in the experiment. It is probable that the rate of TCE dissolution within the column was not the major factor in the movement of TCE through the columns, since the previously estimated residence times for the columns were 15 and 30 days for 100 and 50 ml/day water application rates, respectively.

Effluent pH Values. Effluent pH was measured on all columns on an approximately weekly basis with results listed in Tables B13 and B14. Table 32 summarizes the pH range and

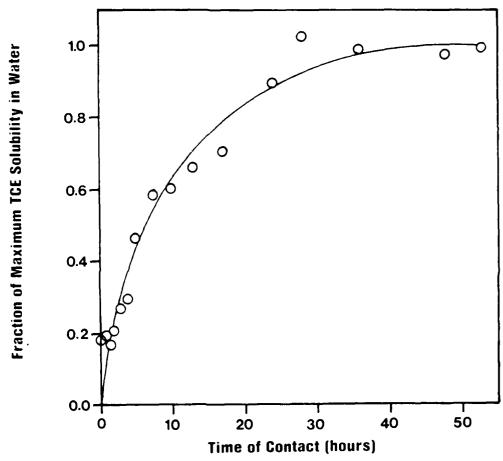


Figure 23. Time of Saturation for TCE and Water.

Table 32. Maximum, Minimum, and Mean pH for Soil Column Effluents.

Column		No. of		
	Maximum	pH Minimum	Mean	Measurements
Chalmers	Soil			
Cl	6.91	5.52	6.25	18
C2	6.72	5.32	6.20	18
C3	6.74	5.70	6.28	18
C4	6.72	5.83	6.23	18
C5	7.19	5.62	6.41	18
C6	7.08	5.82	6.40	18
C7	7.49	6.19	6.72	16
C8	7.21	5.85	6.48	18
C9	7.30	6.12	6.67	18
C10	7.11	5.90	6.37	6
C11	7.39	5.80	6.58	18
C12	7.59	5.76	6.50	18
Control	7.33	5.92	6.34	18
Russell S	<u>oil</u>			
R1	7.23	5.62	6.39	18
R2	6.81	5.41	6.23	18
R3	7.37	5.74	6.35	18
R4	7.16	5.81	6.44	18
R5	7.23	5.71	6.33	18
R6	6.83	6.16	6.40	18
R7	6.30	6.08	6.18	5
R8	7.16	5.83	6.30	18
R9	7.25	5.97	6.50	18
R10	6.67	5.84	6.19	18
Rll	7.21	5.90	6.35	18
R12	6.82	5.95	6.31	5
Control	6.72	5.87	6.28	18

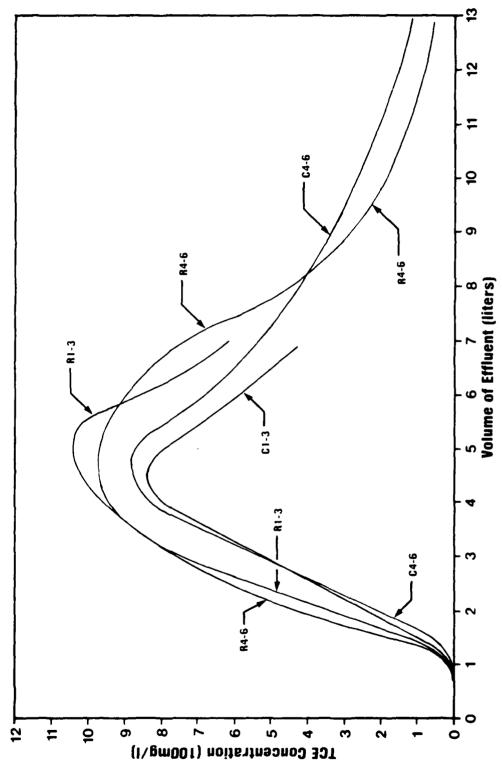
Columns R7 and C10 removed from service on day Notes: l. 44.

Column R12 removed from service on day 45. Column C7 removed from service on day 122. 2.

mean for each of the columns over the entire study. A review of the individual measurements indicates no particular trend; however, all mean pH values were higher than that of the applied water (pH 5.5-6.0). In addition, there was no particular trend for pH values among columns within a specific group. Since the soil pH values listed in Table 15 are all slightly acid or just slightly basic, it was probable the pH of the effluents was largely affected by the complex soil:water interactions as discussed in the Literature Review.

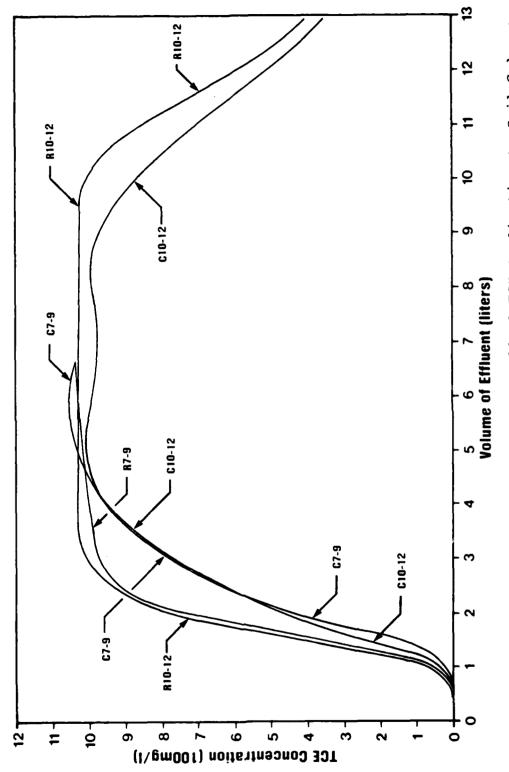
Comparison of TCE Elution Patterns

The factors which varied between the columns in the elution studies were soil type, water application rate, and mass of TCE applied. Effects of these factors are compared in Figures 24-29. To construct these figures, the composite elution curves for the specific column groups of Figures 15-22 were replotted onto collective plots based upon soil type, water application rate, and TCE loading. Therefore, to assess the effects of one factor, such as TCE loading, one must study the collective plots based upon the other two factors, soil type and water application rate. these factors will be discussed separately, based upon the column conditions of Table 22 of the Preliminary Investigations.



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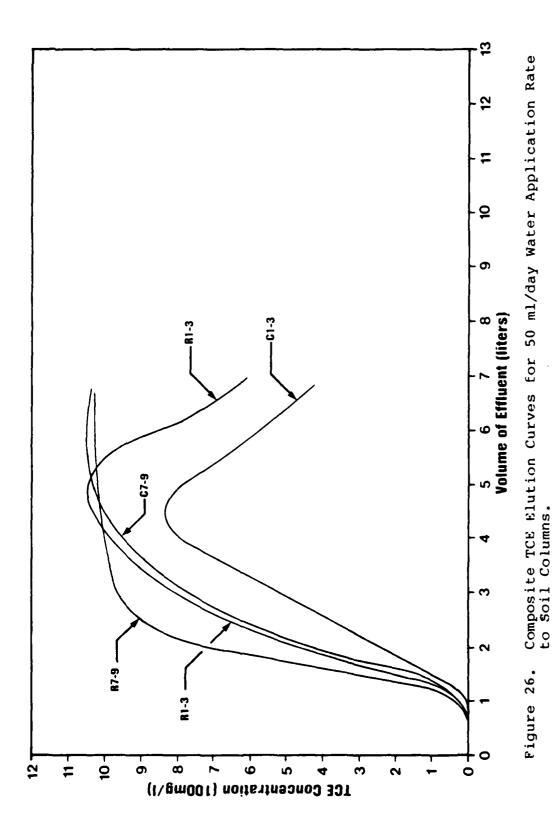
Composite TCE Elution Curves for 5 ml TCE Application to Soil Columns. Figure 24.

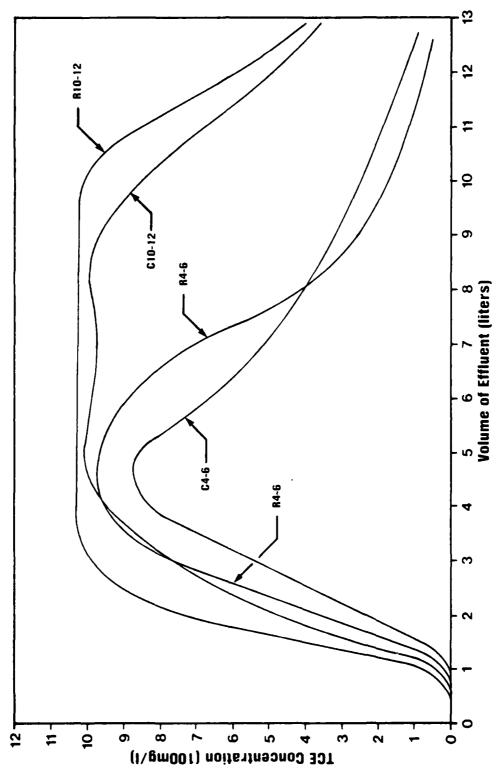


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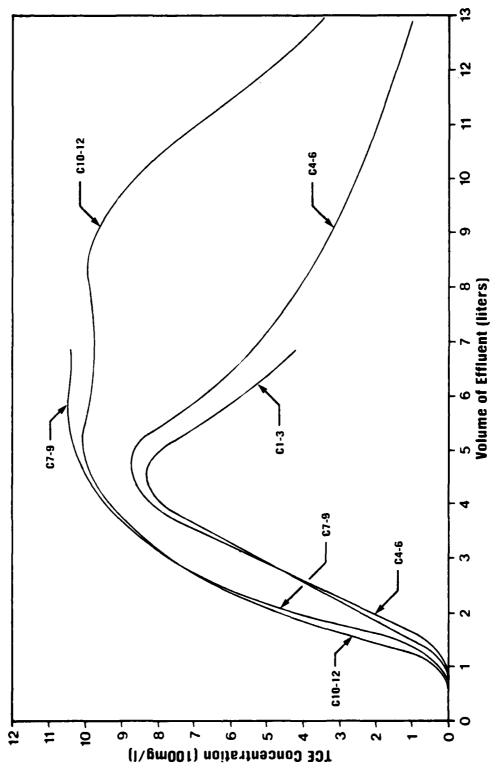
Composite TCE Elution Curves for 10 ml TCE Application to Soil Columns. Figure 25.





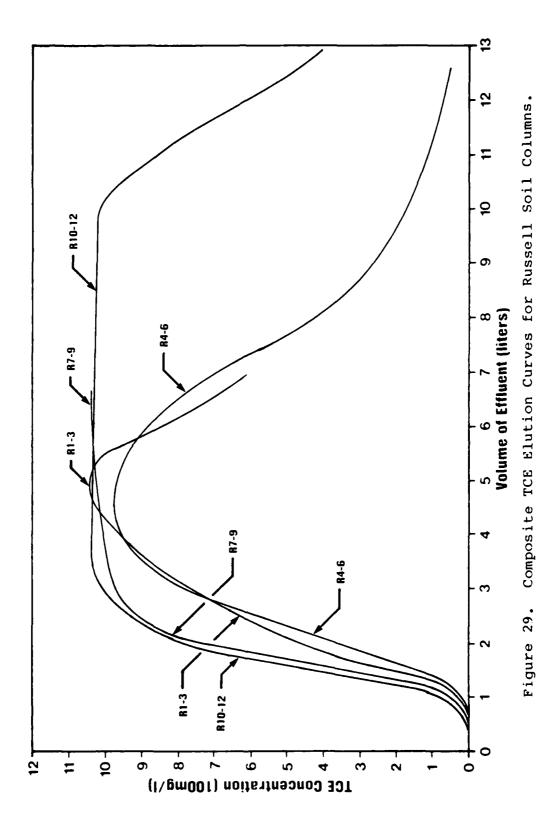
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Composite TCE Elution Curves for $100~\mathrm{ml/day}$ Water Application Rate to Soil Columns. Figure 27.



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Composite TCE flution Curves for Chalmers Soil Columns. Figure 28.



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Soil Type

Table 17 lists the calculated composite organic carbon content of Chalmers soil as 1.4% and that of Russell soil as 0.53%. Other soil parameters are listed in Tables 15 and 16.

The elution curves show the Chalmers soil initially retarded the movement of TCE more significantly than did the Russell soil. This result was more pronounced with the 5 ml TCE loading than with the 10 ml TCE loading. For instance, in Figure 24, the initial stages of the elution curves show lower effluent concentrations for Chalmers soils than for Russell soils at corresponding effluent volumes for 50 ml/day and 100 ml/day application rates. For the latter stages of the 100 ml/day application rate curve, however, the Chalmers soil exhibited higher TCE concentrations. These same results were also indicated by Figures 27 and 28.

Elution curves for the 10 ml TCE loading show slightly less difference between the soils than did the 5 ml TCE loading curve. As shown in Figure 25, the initial appearance of TCE in the effluent came at approximately the same effluent volumes for the different column groups. Both soils exhibited quite similar rates of increase in effluent TCE concentration. These rates of increase are greater than those exhibited by the 5 ml loading. The Russell effluent reached an almost constant effluent TCE concentration which

only decreased from 1,040 to 1,030 mg/l over 6.3 l of effluent. The Chalmers soil exhibited a slight drop in its broad peak or hump which lasted over only 4.0 l of effluent. Concentration levels on the broad peak of the Chalmers elution curve varied from 970-1,020 mg/l. Additionally, the concentration levels of the Chalmers curve (for 100 ml/day) began to decline at a lower effluent volume with an apparent smaller rate of decline when compared to Russell soils.

Figures 26 and 27 also indicate the greater retardation of TCE by Chalmers soil. In these figures, for corresponding soil and water application rates, the elution curves for 5 ml loading show lower TCE concentrations at all points than do the 10 ml loadings. However, in the early stages of both figures, the elution curves for the Russell 5 ml TCE loading closely compared with the curves for the Chalmers 10 ml TCE loading.

from the adsorption isotherms, the adsorptive capacity of the Chalmers soil was found to be greater than that of the Russell soil for both particle sizes studied. In the column studies, the effect of particle size was not considered although soil analyses of Table 15 indicated comparable size distributions of the sand, silt, and clay fractions of the two soils. Consequently, it was consistent with the findings of others (38,55,65,77,79) that the organic carbon content of the two soils was responsible for

the difference in TCE elution through the columns. In this case, the Chalmers soil exhibited greater retardation of TCE movement.

Water Application Rate

The effects of water application rate are graphically shown in Figures 24,25,28, and 29. For the 5 ml TCE loading of Figure 24, the initial stages of elution to maximum TCE concentrations were similar for both application rates (50 and 100 ml/day) for the two soils. Once the elution curves reached maximum concentration, the similarity slightly deviated in the latter stages of elution.

For columns R1-3 (50 ml/day), the maximum concentration reached 1,050 mg/l. This was greater than that for R4 (100 ml/day) which reached 970 mg/l. The converse was true for the Chalmers soil; columns C4-6 (100 ml/day) exhibited a maximum TCE concentration of 880 mg/l while the maximum for columns C1-3 was lower at 840 mg/l. Both of the curves declined at approximately the same rates, separated only by the difference in maximum concentration. Conversely, the elution curve of columns R1-3 declined more rapidly than that for columns R4-6 which showed a broader peak than did columns R1-3.

The differences shown by the 5 ml TCE loading were not apparent in the curves of Figure 25 for the 10 ml TCE loading. There was little variation in elution between the 50 and 100 ml/day water application rates for either soil.

However, the elution curves for the 50 ml/day rates had not yet begun to decline when the study was terminated, so the shape or pattern of the curves in decline could not be determined.

The data shown in Figures 24,25,28, and 29 are graphical indications that the water application rates of this study did not affect the elution of TCE trom the soil columns for either soil or TCE loading studied. As discussed in the Literature Review, Schwarzenbach and Westall (77) found significant differences between pore water velocities of 8.7×10^{-4} cm/sec and 1.0×10^{-2} cm/sec for adsorption: desorption studies in columns.

Pore water velocities for the 50 and 100 ml/day application rates of this study were calculated according to Schwarzenbach and Westall (77) as shown in Appendix A. For the Chalmers columns, the calculated average pore water velocities were 2.8 x 10 $^{-5}$ cm/sec and 5.7 x 10 $^{-5}$ cm/sec for 50 and 100 ml/day application rates, respectively. For the Russell columns, the calculated average pore water velocities were 3.0 x 10 $^{-5}$ cm/sec and 6.0 x $^{-5}$ cm/sec for 50 and 100 ml/day, respectively. Since the pore water velocities were calculated, not measured, they were approximate values only. In addition, since the water application and effluent collection did not always take the full 24 hours of each day, the actual pore water velocities probably varied during the course of the day. Regardless,

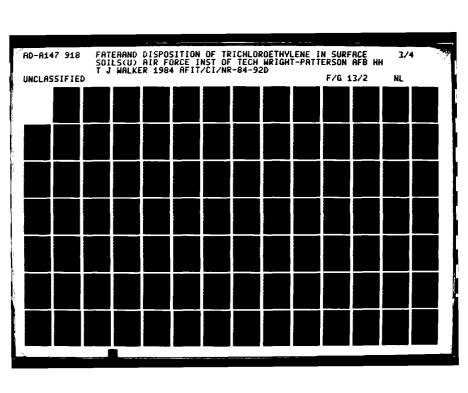
the caculated velocities can be used as a basis for comparison to the work of others.

In this study, the pore water velocities varied only by a factor of two while those of Schwarzenbach and Westall (77) varied by a factor of 11.4. In addition, their lower velocity was 14.7 times greater than the high velocity of this study. Consequently, while comparison between the two studies was not applicable, it is apparent that higher velocities than those of this study are necessary to effect a difference in adsorption due to water application rate.

The water application rates of 50 ml/day and 100 ml/day represent 0.43 and 0.86 inches of rainfall per day. Consequently, the pore water velocities shown in this study are closer to that for natural continuous that that shown by Schwarzenbach and Westall (77). Rainfall, then, should cause no effect due to pore water velocity. However, when considering the time of adsorption previously discussed and the lack of effect of flow rate, it is probable that local equilibrium (as defined in the Literature Review) was reached in all soil columns.

Amount of TCE Applied

As expected, the elution of TCE was more pronounced for the columns loaded with 10 ml of TCE than for those loaded with 5 ml of TCE. This effect was found for both soils as best shown by Figures 28 and 29. Of the two soils, the Russell columns exhibited less difference in elution for the





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two different TCE loadings. This was shown by the fact that for both loadings on Russell soils, the maximum TCE concentrations differed only by 70 mg/l whereas the maximum concentrations for Chalmers soil differed by 210 mg/l. In addition, as previously discussed, free or undissolved TCE was found in the effluent of column R7 but was not found in any other effluents. This point was significant because during a large portion of the study, the columns loaded with 10 ml TCE had constant maximum TCE concentrations only slightly less than 1,100 mg/l, the maximum solubility of TCE in water.

A plausible explanation for the high constant effluent concentrations can be drawn from results of tests previously discussed. The adsorption isotherms indicated increasing adsorption at high concentrations. Hamaker (30) indicated adsorption at chemicals applied directly to the soil can be significantly higher than adsorption of chemicals from This aspect was especially apparent from calculated X/M and X values of Table 25 which indicated the maximum adsorptive capacities for the columns at various TCE concentrations. For instance, in extrapolating the isotherm to a TCE concentration of 1,100 mg/l (maximum solubility of TCE), Table 25 indicates the maximum TCE which could be adsorbed by one of the columns was 6.103 q (4.2 ml). Since the TCE loadings were 5 ml (7.3 g) and 10 ml (14.6 g), free or undissolved TCE should have been detected in the effluents of columns other than R7.

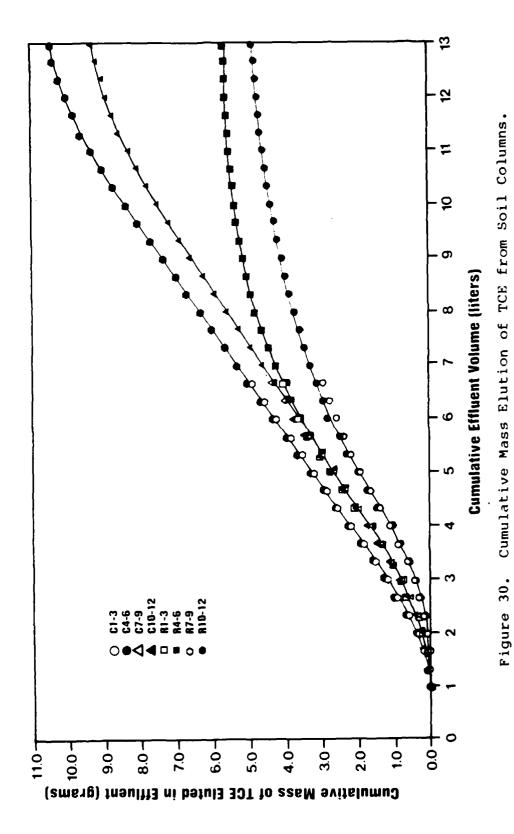
The increased mobility of TCE at the higher loadings can be theorized as due to several factors. In one respect, it was possible that the upper layers of soil strongly adsorbed much of the applied TCE with subsequent elution by the applied water at a constant rate near the maximum solubility As the initially free TCE and subsequent TCE solution traveled through the soil, the TCE may have further adsorbed onto the soil until all adsorption sites were saturated. Once the adsorption sites were saturated, the TCE in solution could have moved through the soil with no further adsorption occurring. In the case of the higher TCE loadings, the adsorption sites throughout the columns became saturated more quickly and the higher TCE concentrations appeared in the effluent at smaller effluent volumes. as the upper levels of adsorbed TCE gradually desorbed, equilibrium concentrations decreased at points throughout thus effectively lowering effluent TCE concentrations.

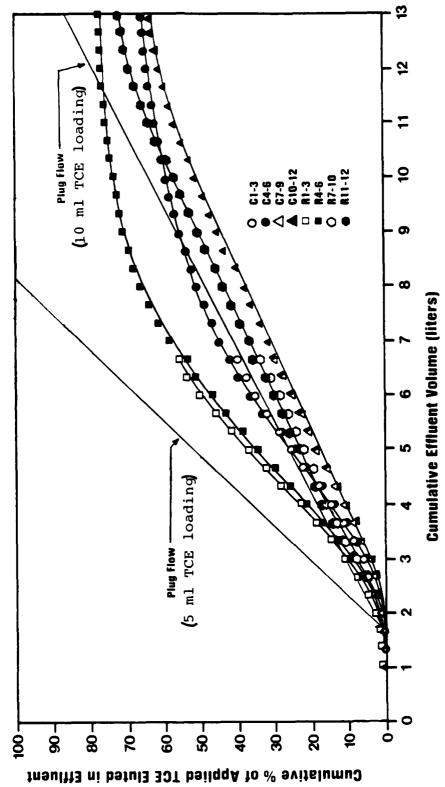
Cumulative TCE Elution

A comparison of the cumulative TCE elution patterns for the soil columns provided additional evidence that adsorption of TCE had occurred within the soil columns. The cumulative elution curves of Figures 30 and 31 were constructed in the following manner:

- 1. The effluent TCE concentrations from the composite elution curves of Figures 15-22 were recorded at 0.33 l increments of cumulative effluent volume (Table Bl5, Appendix B).
- 2. The area under the composite elution curves represented the amount of TCE eluted. Those areas were determined by use of Simpson's Approximation to the data of Table Bl5. The corresponding incremental cumulative mass of TCE eluted for each composite column group determined in this manner is listed in Tables Bl6 and Bl7.
- 3. The percent TCE eluted in the column groups (Tables B16 and B17) was determined on the basis of the cumulative mass of TCE eluted and the corresponding mass of TCE applied to each particular column group. This information was plotted in Figures 30 and 31.

Figure 30 illustrates several findings previously discussed. No difference in elution based solely upon water application rate was shown for any of the corresponding column groups. Additionally, the higher organic soil (Chalmers) showed a higher retardation capacity then did the lower organic carbon soil (Russell). Also, the initial cumulative elution of TCE from Russell soil loaded with 5 ml TCE was nearly identical to that of the Chalmers loaded with 10 ml TCE. These findings indicate the Chalmers soil had a





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Cumulative Percentage Elution of TCE from Soil Columns. Figure 31.

greater capacity than the Russell soil to retain the TCE at both 5.0 and 10.0 ml TCE loadings.

Figure 31 illustrates the same findings of Figure 30. It also compares the percentage elution to that which could be expected from non-adsorption of TCE in a plug flow reactor (PFR) of volume equal to the approximate pore volume of the two different type soil columns. Data used to plot the experimentally determined curves of Figure 31 are contained in Table B18.

The PFR curve was determined in the following manner. No elution of TCE was considered until one approximate pore volume, 1.66 l(average of pore volumes for Russell and Chalmers soil). After one pore volume, the TCE effluent concentration was considered saturated at 1100 mg/l. This concentration was considered to continue until all TCE applied (either 5 or 10 ml) had eluted from the column. Consequently, TCE was considered eluted at the rate of 1100 mg/l in the effluent (1.1 g/l) or 0.75 ml/l. For the 5 ml TCE loading, the percentage elution rate was 15% TCE applied/l effluent. For the 10 ml TCE loading, the % elution rate was considered 7.5% TCE applied/l effluent after l pore volume. Consequently, Figure 31 shows the cumulative percentage elution rate of TCE from the soil columns as considered for both the 5 and 10 ml TCE loadings.

For the 5 ml TCE loading, 100% of the TCE would be eluted by 8.28 l effluent for a PFR. For the 10 ml loading, 100% of

the effluent would be eluted by 14.9 l for a PFR. Theoretically, no TCE would have appeared in the effluent before l calculated pore volume because of the definition of a plug flow reactor.

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Comparing theoretical PRF elution curves with the experimentally determined elution curves, one sees that the steps are quite similar. However, the experimentally determined curves were dissimilar to the theoretical curves in that the theoretical curves indicate a higher percentage TCE elution than do the experimental curves for the same effluent volumes. Since the theoretical curves assumed a non-reactive species, this dissimilarity is not surprising because the batch isotherms had shown that TCE was, in fact, adsorbed from solution and was not a non-reactive species as assumed with a PFR.

Biodegradation Studies

As discussed in the Literature Review, TCE has been shown to be biodegradable. Within this investigation, several different studies and analytical tests were conducted to determine if biodegradation was a major factor in the fate of TCE within the soil columns.

Nutrient Addition

Alexander (1) states that nitrogen is the key nutrient required for biological degradation of organic compounds in soil environments. To determine if TCE biodegradation could be enhanced with nutrient addition, a dilute solution of ammonium hydroxide was added to one column of each column

group beginning on Day 75. The concentration of ammonia as nitrogen was 10 mg/l. This concentration was chosen based upon the theoretical Chemical Oxygen Demand (COD) 0.54 mg COD/mg TCE (calculated in Appendix A). approximate theoretical COD: N requirement 40:1 (1,27,29), the 10 mg/l ammonia nitrogen would satisfy the nitrogen requirement of 761 mg/l TCE. From Figures 15-22, the effluent TCE concentrations ranged from 500-900 mg/l at the start of nutrient addition (Day 75). Ammonia addition to selected columns (C1,C5,C7,C11,R1,R4,R8, and R10) was continued through Day 100. During this period and the subsequent 15 or 30 day residence time after nutrients were discontinued, no evidence was apparent in Figures 15-22 to indicate the effluent TCE concentrations in enhanced columns were significantly lower than TCE concentrations from the other columns within the groupings.

The ammonia nitrogen concentrations in the effluent from Day 71 through Day 122 are listed in Table B19 of Appendix B. These results indicate the nutrient enhanced columns generally passed the ammonia through the soil with very little depletion as shown by the maximum effluent values of 8.0-12.0 mg/l for the enhanced columns. The corresponding non-enhanced columns maintained generally constant ammonia nitrogen concentrations of approximately 0.3-0.7 mg/l during the same period with no particular pattern or trend for

effluent concentration. Generally, the ammonia concentration in the effluent of non-enhanced columns was higher than that for the control columns. No attempt was made to determine mean ammonia concentrations or to compare maximum or minimum concentrations because: (1) the ammonia concentrations were not determined for every effluent on each sampling run; and (2) since ammonia was added to the column with a lag time before it appeared in the effluent, a mean concentration would have no significance for comparison to non-enhanced columns.

the nutrient addition, nitrate concentrations were also determined on the column effluents. Results are shown in Table B20 of Appendix B. the non-enhanced columns showed effluent levels of 0.2-0.5 mq/l nitrate nitrogen. The nitrate levels of the enhanced column effluents were higher, having increased approximately 0.5 mg/l by the end of the enhancement period, Day 100, to approximately 0.7-1.0 mg/l. The control columns (to which no TCE had been applied) had nitrate nitrogen levels of 0.42-0.90 mg/1. These levels were higher than those of the non-enhanced columns. For the same reason stated for the ammonia concentrations, no attempt was made to compute a mean or to compare maximum and minimum values.

Nitrite nitrogen was measured on the control columns on Day 64 and on all columns on Days 73 and 78. Nitrite was

not detected in any of the effluents on these days and no further analyses were conducted.

TCE requires initial dechlorination of the molecule (releasing chloride ions) before it can be biologically degraded (26,46). Complementary to the ammonia and nitrate analytical tests, the chloride levels of the effluents were determined during the period Day 66-Day 127. Table 33 summarizes these measurements as contained in Table B21. Compared to the control columns, all TCE laden soil columns had higher effluent chloride levels over the analytical period. Except for column C1, all nutrient enhanced columns showed mean chloride concentrations 2.0-6.0 mg/l higher than non-enhanced columns. This indicated that some form of TCE degradation had probably occurred within the columns.

The theoretical amount of TCE that would have to be degraded to produce the chloride levels found could calculated. Since chlorine represents 80.95% of the molecular weight of TCE (15,45,76), complete dechlorination and degradation of 1.0 mg of TCE would result in 0.81 mg of chloride. Conversely, 1.0 mg of chloride would represent complete dechlorination and degradation of 1.24 mg TCE. Consequently, the 2.0-6.0 mg/l difference in chloride level between enhanced and non-enhanced columns would indicate only a 2.5-7.4 mg/l difference in effluent TCE concentrations. This slight difference was significant and could neither be accounted for in composite

Table 33. Summary of Soil Column Effluent Chloride Measurements.

	Chlorides, mg/l						
Column	Max.	Min.	Mean	Std. I	Dev.	**Corr. Mean	
Chalmers	Soil						
*C1	9.6	1.9	5.3	2.33	2	3.3	
C 2	6.3	3.7	5.1	0.90	0	3.1	
C3	5.7	2.4	4.0	1.03		2.0	
C 4	4.8	2.2	3.4	0.90	6	1.4	
*C5	8.5	2.8	6.0	2.08	В	4.0	
C 6	4.2	<1.0	2.9	1.19	5	0.9	
*C7	12.2	4.1	8.6	2.60	0	6.6	
C8	3.5	1.1	2.5	0.7	l	0.5	
C 9	4.1	1.0	2.2	1.13		0.2	
C10	Removed	from ser	rvice on	Day 44.			
*C11	12.1	3.8	8.3	2.36	6	6.3	
C12	4.8	1.4	3.1	1.16	6	1.1	
Control	3.2	1.0	2.0	0.7	1	-	
Russell S	<u>oil</u>						
*R1	10.8	4.8	7.5	1.90	6	5.9	
R2	4.6	1.3	2.7	1.03		1.1	
R3 ·	3.2	<1.0	2.3	0.76	6	0.7	
*R4	10.2	3.6	6.0	1.90	6	4.4	
R 5	4.6	1.6	3.2	0.98	В	1.6	
R 6	4.4	<1.0	2.7	1.24	4	1.1	
R 7	Removed	from ser	rvice on	Day 44.			
*R8	10.6	2.8	6.4	2.2	1	4.8	
R9	5.3	1.8	3.2	1.14		1.6	
*R10	8.5	1.4	6.0	2.4	4	4.4	
R11	4.2	1.2	2.5	1.03	2	0.9	
R12	Removed	from ser	rvice on	Day 45.			
Control	3.1	<1.0	1.6	0.60	6	-	

^{*}Indicates columns to which 10 mg/l ammonia - N added to elution water.

^{**}Corr. Mean = Corrected Mean = Mean of Column - Mean of Control.

elution curves of Figures 15-22 nor differentiated in individual analyses due to the random error of the analytical tests. The effect of less than complete dechlorination will be discussed later.

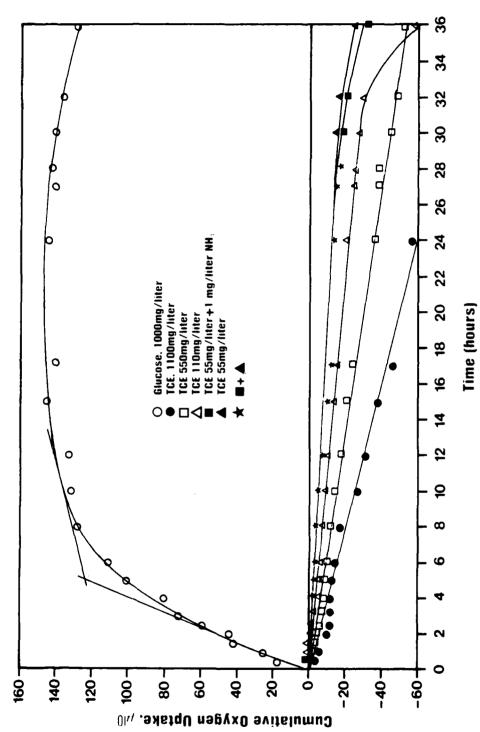
During the 26 days of nutrient enhancement, either 50 ml/day or 100 ml/day of 10 mg/l solution of ammonia nitrogen were added to the soil columns. In terms of total ammonia added to the columns, this equated to either 13 mg (50 ml/day) or 26 mg (100 ml/day). As previously discussed, 10 mg of ammonia nitroyen would theoretically satisfy the nutrient requirements of 761 mg of TCE. Consequently, 13 mg would theoretically satisfy 989.3 mg of TCE while 26 mg would theoretically satisfy 1,987.5 mg of TCE. If these TCE amounts of were to be considered completely dechlorinated and degraded, then the respective amounts of chloride released would be 800 and 1,600 mg. These chloride amounts can be correlated to the flow rates. During the enhancement period, either 1.3 1 (50 ml/day) or 2.6 1 (100 ml/day) of water were applied to the columns. the theoretical chloride concentration (if all available added nitrogen was used) should have reached 615 mg/l. Αt least 800 mg (500 ml/day) or 1,600 mg (100 ml/day) of chloride would then have eluted during the enhancement period plus one residence time. Chloride measurements during this time period did not indicate levels or quantities of chlorides of this magnitude. Nutrient

enhancement, then, provided very little additional biological degradation of TCE within the soil columns. Because of this and findings from Warburg studies discussed later, nutrient enhancement was stopped at Day 100.

Warburg Respirometer Studies

Metry were conducted concurrently with the column elution studies and nutrient enhancement of selected soil columns. The purpose of the respirometry studies, as discussed in Materials and Methods, was to determine relative rates of aerobic TCE degradation by various profile depths of the soils under study. These studies were not intended to determine the exact amount of TCE degradation. After a testing protocol was developed using a glucose solution as substrate, actual work using a TCE solution with an uncontaminated soil sample was attempted according to the procedure described in Materials and Methods.

The initial respirometric study used soil from a 2.5 inch depth of an extra Chalmers column which had not been used in the column elution studies. This soil sample had TCE applied considered never had to it and was "unacclimated". Glucose, an easily degradable material, was used as a substrate to indicate biological activity. solutions ranging from 55-1,100 mg/l were used as test substrates. The results of the test are plotted in Figure 32 for results shown in Table Dl of Appendix D. The table



Warburg Oxygen Uptake for Unacclimated Chalmers Soil Supplemented with TCE for 2.5 Inch Depth. Figure 32.

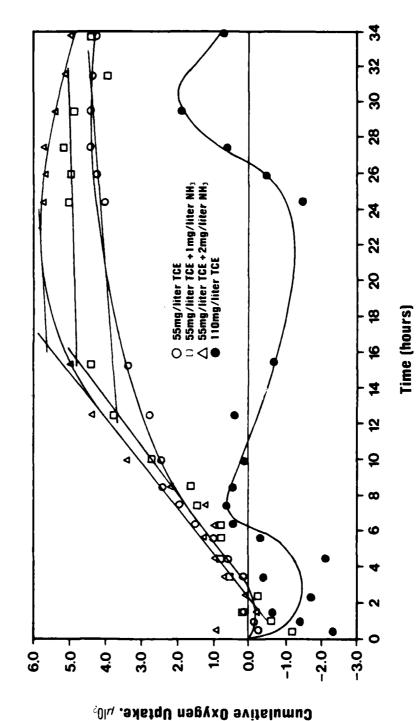
and figure show the cumulative oxygen utilization in microliters (ul) to be negative when corrected endogenous utilization for all TCE solutions tested. The glucose showed a postitive oxygen utilization, so the test considered to have been run under satisfactory conditions. Additionally, the total cumulative endogenous oxygen utilization was 171.51 ul in an approximate linear fashion. Divided over the period of the test 36 hours, and the mass of soil used in the test, 2.70 g, the endogenous rate was approximately 1.76 ul/g soil/hr. Converting this oxygen utilization to carbon dioxide production. then 1.76 ul/q soil/hr of carbon dioxide was produced. On a mass basis, this converts to 3.46 ug/g soil/hr or 83 ug/g/day of This production rate closely approximated carbon dioxide. that reported by Alexander (1). He found typical carbon dioxide production for mineral soils in the field commonly ranged from 5.0-50 ug/g soil/day. Consequently, because of this and the degree of glucose respired by the soil, the test was considered to have been representative of normally expected conditions.

From this initial test with unacclimated soil, it was determined that the levels of TCE tested were inhibitory to degradation over the time period used. Even nutrient enhancement of a 55 mg/l TCE concentration showed no evidence of oxygen utilization. Since degradation of anthropogenic compounds such as TCE may require induction of

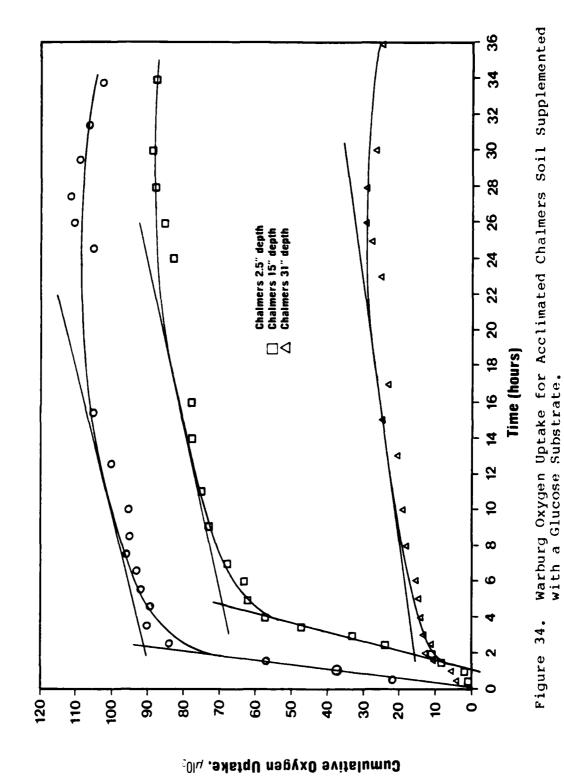
enzymes before the compound can be biodegraded (1,27,46), additional testing was conducted with "acclimated" soil.

Acclimated soil was obtained from two soil columns which had been removed from the elution studies because of breakage of the glass tubing. These columns were C10 for Chalmers soil and R12 for Russell soil. During the initial two weeks after being removed from service, the columns had been maintained in the column room. After this period, the columns were extruded, sectioned, wrapped in aluminum foil, and refrigerated at 4°C. Soil from these sections was used in the acclimated studies.

The first test with acclimated soil was conducted with Chalmers soil from a 2.5 inch depth. Results are shown in Table D2 and Figures 33 and 34. This test appeared successful so subsequent tests were run with other Since these tests were to be used on a acclimated soils. comparative basis, the total oxygen uptake for each solution tested was determined when possible. This was determined by intersecting the linear portion of the uptake curve with the upper portion of the same curve as it approached the endogenous rate. This total oxygen uptake was converted to a percentage of substrate respired with the theoretical TCE:oxygen relationship calculated in Appendix A. This same relationship was used to convert the rate of oxygen uptake to a rate of TCE respiration. The rate of oxygen uptake was determined from the inital linear portion of the



Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 2.5 Inch Depth. Figure 33.



Č

cumulative oxygen uptake curve. The total oxygen uptake and percentage respired were similarly determined for glucose according to the glucose:oxygen relationship calculated in Appendix A. These data are contained in Tables 34,35, and 36.

For the 2.5 and 15 inch depth acclimated samples, the Chalmers soil (1.4% organic carbon) showed a greater total oxygen uptake and percentage respired for the glucose substrate than shown by the Russell soil (0.53% organic carbon). For the same parameters at the 31 inch depth, the Russell soil showed higher results. However, at none of the depths tested was the corresponding difference between values for the two different soils great. For Chalmers soil, the glucose degradation required no lag time and was complete (rate returned to endogenous) within two to four hours. The Russell soils required a lag time of approximately two hours with degradation complete in six to ten hours.

In all soils, the 110 mg/l TCE solution and the 550 mg/l TCE solution (Russell, 2.5 inch depth) produced negative cumulative oxygen utilization. Since this indicated an inhibitory effect, no total uptake or rate of respiration could be determined. These same parameters also could not be determined for any of the TCE solutions tested with the soils from 31 inch depths. Testing with soils from these depths proved to be too sensitive for the degree of accuracy

Table 34. Total Oxygen Uptake from Acclimated Soil Warburg Studies When Supplemented with TCE or Glucose.

	Total Oxygen Uptake, ul					
Soil Type and Depth, Inches	Glucose, 500 mg/l	TCE, 110 mg/l	TCE, 55 mg/l	TCE,a 55 mg/l	TCE, b 55 mg/l	
Chalmers Sc	oil			- · · · · · · · · · · · · · · · · · · ·		
2.5	91	nd	3.6	4.8	5.6	
15.0	69	nd	2.2	2.2	2.2	
31.0	16	nd	nd	nd	nd	
Russell Soi	<u>.1</u>					
2.5	79	nd ^C	3.4	3.6	4.1	
15.0	53	nd	2.2	2.6	2.4	
31.0	21	nđ	nd	nd	nd	

Notes: aSolution contained 1 mg/l ammonia nitrogen.

bSolution contained 2 mg/l ammonia nitrogen.

CTCE solution = 550 mg/l.

nd - Unable to be determined.

Table 35. Percent Substrate Respired from Acclimated Soil Warburg Studies When Supplemented with TCE or Glucose.

	Percent Substrate Respired					
Soil Type and Depth, Inches	Glucose, 500 mg/l	TCE, 110 mg/1	TCE, 55 mg/l	TCE, a 55 mg/l	TCE, b 55 mg/l	
Chalmers So	<u>i1</u>		· · · · · · · · · · · · · · · · · · ·			
2.5	24.5	nđ	17.3	23.1	26.9	
15.0	18.6	nd	10.4	10.4	10.4	
31.0	4.3	nd	nd	nd	nd	
Russell Soi	1					
2.5	21.3	ndc	16.4	17.3	19.7	
15.0	14.3	nd	10.8	12.5	11.8	
31.0	5.6	nđ	nd	nđ	nd	

Notes: aSolution contained 1 mg/l ammonia nitrogen.

bSolution contained 2 mg/l ammonia nitrogen.

CTCE solution = 550 mg/l.

nd - Unable to be determined.

Table 36. Rate of TCE Respiration from Acclimated Soil Warburg Studies When Supplemented with TCE.

	Rate of TCE Respiration, ug TCE/g soil/hr					
Soil Type and Depth, Inches	TCE, 110 mg/1	TCE, 55 mg/l	TCE, a 55 mg/l	TCE, b 55 mg/l		
Chalmers Soil						
2.5	nđ	0.39	0.39	0.39		
15.0	nđ	0.26	0.26	0.26		
31.0	nd	nd	nd	nd		
Russell Soil						
2.5	ndc	0.39	0.39	0.39		
15.0	nd	0.26	0.26	0.26		
31.0	nd	nd	nd	nđ		

Notes: aSolution contained 1 mg/l ammonia nitrogen.

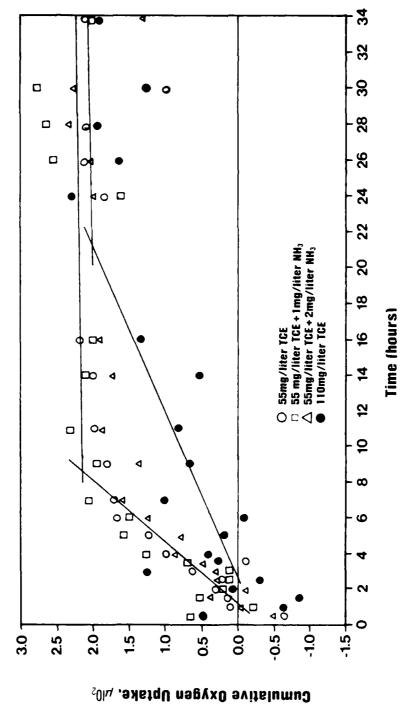
bSolution contained 2 mg/l ammonia nitrogen.

CTCE solution = 550 mg/l.

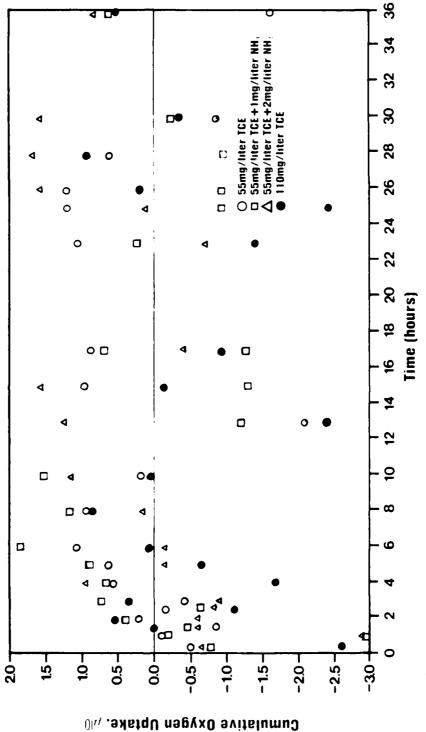
nd - Unable to be determined.

afforded by the Warburg micromanometers. The endogenous rates for the 31 inch depth samples, and their corresponding carbon dioxide production rates appear to fall within the order of magnitude suggested by Alexander (1); however, biological activity of these samples apparently was not enough to provide a significantly different oxygen uptake with the TCE solution to accurately measure the respiration of TCE.

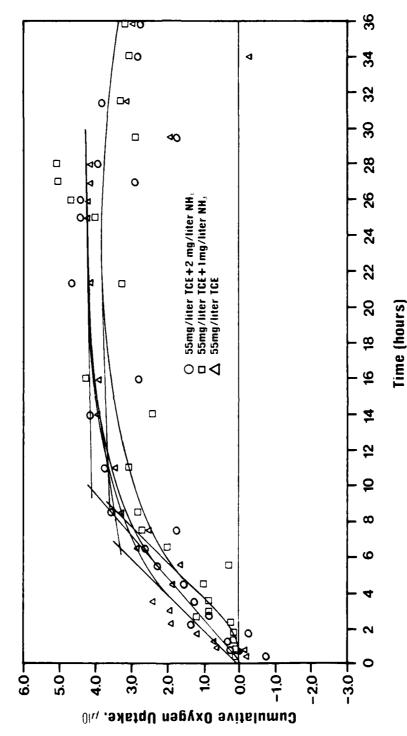
For the 55 mg/l TCE solutions, both soils exhibited higher total oxygen uptake and percentage respired at the 2.5 inch depth than at the 15 inch depth. This decrease with depth was expected since according to Table 7 (1) the concentration of microorganisms decreased with depth. When compared between soils, however, the Chalmers 2.5 inch depth exhibited a higher uptake and percentage of TCE respired than did the Russell 2.5 inch depth. The opposite was true at the 15 inch depth. One possible explanation for this was the concentration of microorganisms proportional to the organic carbon content of the soil (1,27). According to Table 15, the percentage of carbon at the 2.5 inch depth of the Chalmers soil was 3.03% while for Russell soil it was 1.22%. This was a much greater difference than that at 15 inches where the percentage of organic carbon for Chalmers was 0.59% and 0.41% for Russell soil. Consequently, the concentration of microorganisms in the Chalmers soil at 2.5 inches may have been significantly



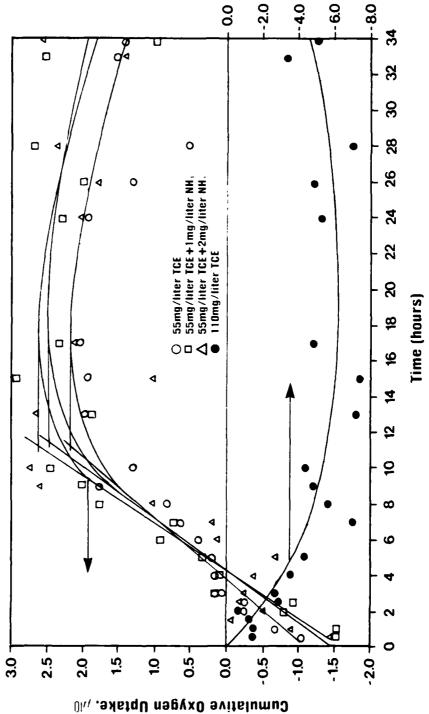
Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 15 Inch Depth. Figure 35.



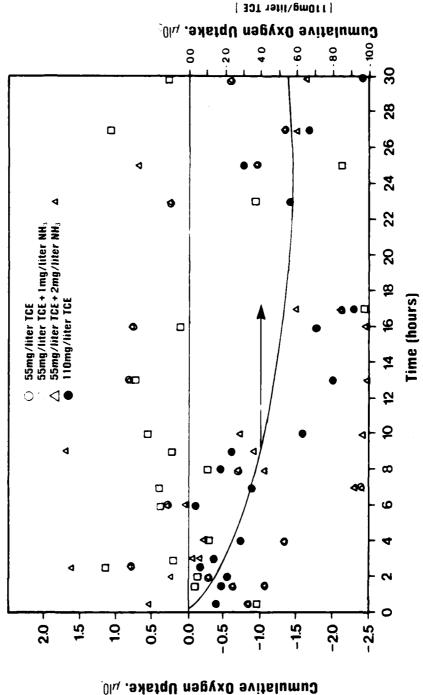
Warburg Oxygen Uptake for Acclimated Chalmers Soil Supplemented with TCE for 31 Inch Depth. Figure 36.



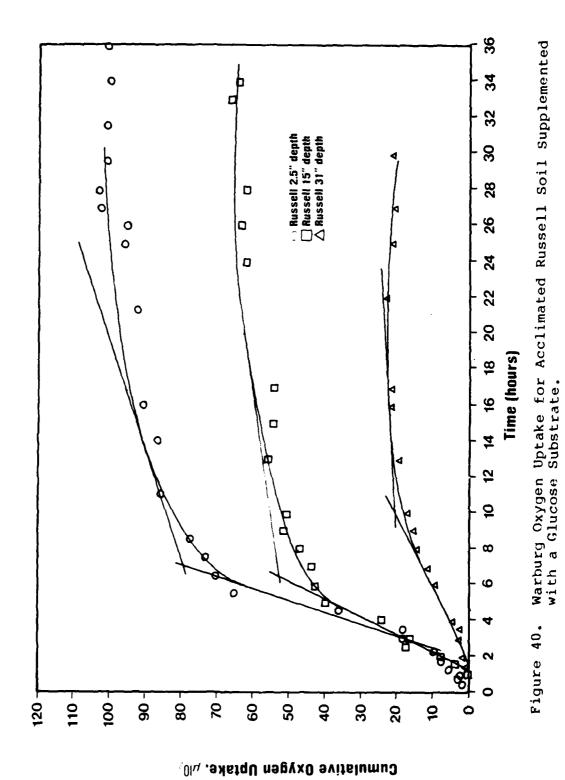
Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 2.5 Inch Depth. Figure 37.



Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 15 Inch Depth. Figure 38.



Warburg Oxygen Uptake for Acclimated Russell Soil Supplemented with TCE for 31 Inch Depth. Figure 39.



greater than that at the corresponding depth for Russell soil. However, with only a slight difference in organic carbon content at 15 inches, there may have been no significant difference in the number of microorganisms at that depth. Additionally, since the types of microorganisms may have varied between the types of soils and depths (1,27,29), no particular significance can be attached to differences between the soils.

The 55 mg/l TCE substrates enhanced with ammonia nitrogen showed slightly higher percentage substrate respired and corresponding total oxygen uptake compared to the non-enhanced 55 mg/l TCE solution. This was evident for the 2.5 and 15 inch depths for each soil. The difference between the l mg/l ammonia and 2 mg/l ammonia enhancement was slightly apparent for the 2.5 inch depth but not apparent for the 15 inch depth. Additionally, the ammonia did not enhance the rate of degradation. Based upon this and the results of the ongoing column nutrient enhancement studies, it appeared this type of nutrient addition did not increase TCE degradation. Consequently, the nutrient enhancement column studies were terminated on Day 100.

As a measure of the validity of the Warburg tests as run in this investigation, the rates of endogenous respiration and the associated carbon dioxide production were calculated for each soil and depth tested. These values are shown in Table 37. As previously discussed, Alexander (1) reported

Table 37. Rate of Endogenous Respiration and Carbon Dioxide Production for Soil Samples from Columns at Various Depths.

Soil Type and Depth, Inches	Rate of Endogenous Respiration, ul O ₂ /g soil/hr	Rate of Carbon Dioxide Production, ug CO ₂ /g soil/day
Chalmers Soil		
2.5ª	1.8	83
2.5	1.4	. 66
15.0	0.9	42
31.0	0.7	33
Russell Soil		
2.5	1.0	47
15.0	0.6	28
31.0	0.5	24

Note: ^aUnacclimated soil. All other soils were acclimated.

the typical mineral soil in the field produces 5.0-50 ug carbon dioxide/g soil/day. The production rates shown in Table 37 closely approach this order of magnitude. Additionally, since field soil would probably be of a lower temperature than the 25°C conditions of the Warburg studies, the values calculated for Table 37 are probably higher than would be expected for the same soils in the field.

Summary

These studies were intended to determine if biodegradation was a major factor in the fate of TCE within the soil columns. It was not intended to be an attempt to determine kinetics or mechanisms of TCE biodegradation. However, several points from the studies were worth discussion.

The pH of the column effluents fell within the range for satisfactory growth conditions as previously discussed. Consequently, pH could not have been an inhibitory factor in the degradation studies.

In neither the column enhancement nor the Warburg studies did nitrogen addition significantly increase TCE degradation. The glucose substrates in the Warburg studies were degraded without added nutrients. This indicated that nutrients were probably not a limiting factor in degradation. There was no concern that other nutrients such as phosphorus could have been limiting since glucose substrates showed significant degradation over the course of the studies for all soils tested.

While the nitrate levels increased in all effluents of nutrient enhanced columns, this was probably because of nitrification of some of the available ammonia. Since the ammonia levels of the nitrogen-enhanced columns eventually approximate influent levels, reached the nitrification did not take place. This could have possibly been due to a lack of oxygen in the soil which would have The soil columns were in a inhibited nitrification. saturated or nearly saturated state for most of the study so quite possibly in an anaerobic or oxygen they were limited condition (1,2). This would explain the slightly elevated nitrate levels in the test columns over those for the control columns. Additionally, in the Warburg studies, oxygen was not a limiting factor since the soil:substrate mixture was constantly shaken to provide sufficient oxygen transfer.

Regardless of whether oxygen was a limiting factor in the column studies, the Warburg studies indicated TCE levels of 110 and 550 mg/l inhibited oxygen utilization even in acclimated soils. Since the effluent TCE concentrations during the column studies reached levels over 550 mg/l, it is probable that very little aerobic TCE degradation took place within the columns. However, as illustrated by the low chloride concentration in the effluents, very little anaerobic degradation could have occurred either, although no anaerobic studies were conducted to confirm this.

Consequently, biodegradation was not considered a major factor in the fate of TCE in this investigation.

Abiotic Degradation

As discussed previously in Biodegradation Studies, effluents from the nutrient enhanced columns generally contained higher chloride levels than effluents from the non-enhanced columns (Table 33). This higher level could have been due not only to biological degradation, but also to abiotic degradation.

In the Literature Review, photodegradation of TCE was discussed. This specific method of abiotic degradation was not accounted for but was considered with other abiotic degradation. Photodegradation of TCE was not considered to be enhanced by the presence of light in the column room for several reasons. First, the lights were on for only two to three hours/day. Secondly, less than half of the column soil surface area was directly exposed to the light since the support rack was mounted directly next to a wall. Consequently, photodegradation of TCE as a specific form of degradation was disregarded.

Two of the initial degradation products of TCE would be cis-1,2-dichlorethylene (cis-1,2-DCE) and trans-1,2-dichlorethylene (trans-1,2-DCE) (62). While these are not the only possible degradation products, these are the ones which would be readily apparent. To determine the possible presence of DCE in the column effluents, the

retention time of the compounds was determined for the GC column, operating conditions, and procedures for TCE headspace analysis discussed in Materials and Methods.

Solutions of cis-1,2-DCE and trans-1,2-DCE were made from reagent grade chemicals from Eastman Chemical Company that had been redistilled in an all glass distillation Based upon headspace analysis, the retention times were 1.22 minutes for trans-1,2-DCE and 1.97 minutes for cis-1,2-DCE. These retention times provided enough separation from the TCE peak of interest (2.2 minutes) so that even in the presence of 880 mg/l TCE, both the cis and trans isomers of DCE in prepared solutions could be detected to a minimum level of 2.0 mg/l. A review of the chromatograms indicated no peaks at the retention times for cis-and trans-1,2-DCE. This indicated these compounds were present at less than 2.0 mg/l throughout the column studies if they were present at all.

Removal of one chlorine from TCE would form one chloride ion plus either trans or cis-1,2-DCE. This reaction shows that for each 1.0 mg/l chloride ion formed from TCE, 2.7 mg/l DCE would be formed. The corrected mean chloride concentrations (Table 33) of the column effluents were generally greater than 1.0 mg/l. Since no DCE was indicated above the 2.0 mg/l detection level, abiotic degradation of TCE to DCE was minimal. If present, though, this degradation would have accounted for less than 1.0 mg/l

chloride in the column effluents. Consequently, biological degradation of TCE, rather than abiotic degradation, was the probable major cause of the additional chlorides found in the TCE test columns compared to the control columns.

TCE Mass Balance

The overall fate and disposition of TCE in the column studies included that which was eluted in the effluents, remained adsorbed on the columns, degraded (biologically and abiotically), and volatilized. Except for volatilization, these fates have been discussed but the total quantities of TCE associated with them have not been presented. This section quantifies the TCE associated with each of these fates and estimates the amount of TCE that volatilized.

TCE Eluted in Column Effluents

The incremental TCE elution was illustrated in Figures 30 and 31 from the data of Tables B16 and B17. Table 38 summarizes the TCE elution for each column group for both water application rates and corresponding final effluent volumes. As discussed previously, these data on elution volumes indicate there was no difference in elution based on flow rate.

TCE Remaining on Soil

The column elution studies were discontinued after 132 days. Soil samples from one column of each column group were then extracted according to procedures listed in

Table 38. TCE Eluted in Soil Column Effluents.

			TCE E	uted :	in Efflue	ent
	Mass of TCE	Water	CEV = 6.	67 1 ^b	CEV = 1:	3.0 1
Column Group	Applied ^a ,	Application Rate, ml/day	Mass, g	&C.	Mass, g	8
C1-3	7.30	50	2.94	40.3	-	_
C4-6	7.30	100	3.10	42.5	4.84	66.3
C7-9	14.60	50	4.38	30.0	-	-
C10-12	14.60	100	4.32	29.6	9.34	64.0
R1-3	7.30	50	4.04	55.3	_	-
R4-6	7.30	100	3.99	54.7	5.66	77.5
R7-9	14.60	50	4.92	33.7	-	-
R10-12	14.60	100	5.08	34.8	10.47	72.5

Notes: aMass based on TCE specific gravity = 1.46.

bCEV = Cumulative Effluent Volume.

C% = % of TCE applied.

Materials and Methods. This extraction determined the mass of TCE that remained on the soil. Samples were taken from 2.5,15, and 30 inch depths which closely corresponded to sampling depths used for the Warburg experiments. Table 39 presents results of the TCE analysis on the depth samples. For all corresponding column conditions, the Chalmers soil retained more TCE than did the Russell soil. This was expected since Table 38 and Figures 30 and 31 had indicated more TCE eluted from the Russell columns than from the Chalmers columns.

The TCE extracted from the soil also included that TCE in solution in the water present as soil moisture. To eliminate the moisture would have required drying the soil samples. This would have resulted in TCE volatilization losses from the soil. No attempt was made to account for this soil moisture TCE content since the liquid TCE concentration was not known at the exact point from which the samples were collected. In this way, the soil moisture TCE was included in the mass balance. Consequently, no attempt was made to differentiate between TCE adsorbed to the soil and TCE present in the soil moisture.

When all columns were disassembled, the base stopper assemblies were checked to determine the integrity of the aluminum foil liners. All liners were intact except for those on columns C4, C6, and R11, which were slightly torn. These tears could have allowed TCE to adsorb to the

stoppers; however, this was not anticipated to be significant since there was no major difference in effluent concentrations between these columns and others of the corresponding column groups tested.

Table 39 indicates the pattern of how TCE was eluted from the upper soil levels through the column by the water applied. Except for column C4, the upper soil layers retained more TCE than the lower soil layers. In all cases, the columns loaded with 10.0 ml TCE showed higher TCE soil concentrations than corresponding columns loaded with 5.0 ml TCE. This could possibly have been due to a higher adsorptive capacity at higher TCE loadings as indicated by the slight upturn of adsorption isotherms at higher TCE concentrations. Additionally, except for the 30 inch depth sample, all Chalmers soils retained more TCE than the corresponding samples of Russell soils. This was expected since the Chalmers soils showed a higher adsorptive capacity based on the batch isotherm studies.

Another indication of increased adsorptive capacity at high TCE loading was the comparison between actual and predicted capacity of the soil columns for TCE. Table 39 lists the calculated mass of TCE that remained on the columns after elution, while Table 40 lists the sum of TCE that was either eluted or retained. A comparison of these values with the predicted maximum adsorptive values, or X values, of Table 25, showed the columns were able to adsorb and retain more than that predicted by the isotherms.

Table 39. Concentration and Mass of TCE Remaining on Soil Columns after Elution.

		Dep	^a Calculated Mass of TCE		
Column		2.5 Inches	15 Inches	30 Inches	on Column, g
Cha	lmers Soi	1			
Cl	mg/g ^b	0.663 0.83	0.346 0.95	0.114 0.16	1.94
C 4	mg/g	0.142 0.18	0.180 0.49	0.086 0.12	0.79
С9	mg/g g	1.70 2.13	1.23 3.37	0.261 0.36	5.85
C12	mg/g g	0.490 0.61	0.281 0.77	0.163 0.23	1.61
Rus	sell Soil	<u>.</u>			
R2	mg/g g	0.327 0.43	0.265 0.76	0.156 0.23	1.42
R6	mg/g g	0.106 0.14	0.080 0.23	0.074 0.11	0.48
R 9	mg/g g	1.29 1.79	0.81 2.81	0.178 0.36	4.96
Rll	mg/g g	0.227 0.30	0.205 0.59	0.109 0.16	1.05

Notes: aCalculated from sum of g's for column.

 $b_{mg/g} = mg TCE/g soil (dry weight basis).$

 $^{\text{C}}\text{g}$ = Calculated mass, in grams, of TCE on segment of soil column as calculated in Appendix A.

TCE Degraded

Previous discussion indicated that the primary chemical degradation products of TCE (cis and trans-1,2-DCE) were not detected at the detection limit of Accordingly, for the purpose of the mass balance, the chlorides associated with the TCE laden columns are attributed to biological degradation. Consequently, to determine the amount of TCE attributed to degradation, the average of the corrected mean chloride concentrations of Table 33 were determined for the non-enhanced columns of each column group. As discussed in Biodegradation Studies, 1.0 mg of chloride represents complete dechlorination and degradation of 1.24 mg TCE. This factor was applied to the average corrected mean chloride concentration and total effluent volume for the appropriate column groups. used to determine the mass of TCE degraded as reported in Table 40.

Volatilization

Table 40 contains the mass balance as determined from the quantities of TCE associated with the previously discussed fates. The loss of TCE due to volatilization was attributed to that which could not be quantified by elution, soil retention, and degradation. While other factors such as glass and gravel adsorption could account for some loss of TCE, these factors were previously found to be

Table 40. TCE Mass Balance for Soil Columns Operated Continuously with Water Application for 132 Consecutive Days.

		Mass of TCE Associated with Fate				Eluted +	
Column Group		Eluted	uted Retained Degraded ^a Volatilized		^a Volatilized	Retained, g	
Chalm	ne r	s Soil					
C1-3	åc gp	2.94 40.3	1.94 26.6	0.02 0.3	2.4 32.8	4.88 66.9	
C4-6		4.84 66.3	0.79 10.8	0.02 0.3	1.65 22.6	5.63 77.1	
C7-9	g &	4.38 30.0	5.85 40.1	0.01 0.1	4.36 29.8	10.23 70.1	
C10-	g	9.34	1.61	0.02	3.63	10.95	
1 ~	ક્ર	64.0	11.0	0.2	24.8	75.0	
Russe	<u> 11</u>	Soil					
R1-3	g %	4.04 55.3	1.42 19.5	0.01 0.2	1.83 25.0	5.46 74.8	
R4-6		5.66 77.5	0.48 6.6	0.02 0.3	1.14 15.6	6.14 84.1	
R7-9	g %	4.92 33.7	4.96 34.0	0.02 0.2	4.7 32.1	9.88 62.7	
R10- 12	g %	10.47 72.5	1.05 7.2	0.02 0.2	3.06 20.1	11.52 79.7	

Notes: aVolatilization attributed to that not accounted for by other fates.

bmass, in grams.

C% of applied TCE.

d Sum of mass of TCE which was eluted and retained on soil, grams. negligible. Consequently, volatilization was determined to be the major fate of the unaccounted for TCE.

Summary

Elution was the major route by which TCE was removed from the columns for the 100 ml/day water application rates. Despite having a restricted headspace, calculated volatilization losses for the columns ranged from 15.6-32.8%. Volatilization of TCE from columns with water application rates of 100 ml/day was less than that from 50 ml/day columns. The reason for this difference was investigated but it is possible the elution of TCE at 50 ml/day allowed the TCE to remain at the top of the soil column longer. This could have provided less of a barrier to volatilization than the 100 ml/day which translocated the TCE deeper into the soil column where volatizilation would have been minimized.

Findings as Applied to an Actual Release to the Environment

This study has shown that high concentrations of TCE can be eluted through 33 inches of soil. However, during the course of this investigation, the equivalent rainfall applied was 0.43 inches/day (50 ml/day) and 0.86 inches/day (100 ml/day) for respective totals of 56.8 and 113.6 inches. These volumes are high for a 132 day period but do indicate the necessity for early discovery and remedial action at TCE release sites.

TCE was shown to be inhibitory to biological activity in unacclimated soil at levels down to at least 55 mg/l. Consequently, biodegradation as a means to restore early detected spill sites may not be feasible but may apply to dilute, aged, or "acclimated" spill sites.

If a release is detected immediately and the soil contains a high level of organic carbon, the TCE may be highly adsorbed and its movement retarded. In this case, consideration could be given to ways to increase the volatilization of TCE. One such method would be to plow or till the site to increase the surface area of soil exposed to the atmosphere. Depending upon weather conditions such as precipitation, temperature, and sunlight, the volatilization for a volatile compound such as TCE may be the major route of disappearance from the soil. Plowing or tilling to increase volatilization may also increase aerobic degradation and photodegradation.

SUMMARY

The fate of trichloroethylene in two different soils under conditions of a simulated spill or discharge was studied by continuous elution of soil columns with water for 132 consecutive days. The soils, Chalmers Silty Clay Loam and Russell Silt Loam, were common soils with similar particle size composition but different organic carbon contents. The Chalmers Silty Clay Loam had a composite organic carbon content of 1.4% while that of the Russell Silt Loam was 0.53%.

TCE was initially applied to the surface of each of twelve columns of each type soil. An additional column of each soil was used as a control. Triplicate columns of each soil were used for four different test conditions: (1) 5 ml TCE, 50 ml water/day; (2) 5 ml TCE, 100 ml water/day; (3) 10 ml TCE, 50 ml water/day; (4) 10 ml TCE, 100 ml water/day. Control columns had no TCE applied but were only eluted with 100 ml water/day. The equivalent rainfall for the water application rates was 0.43 inches/day (50 ml/day) and 0.86 inches/day (100 ml/day). Soil columns consisted of 33 inch long, three inch diameter soil cores extruded into

Pyrex glass tubing. Water was applied by intravenous sets which allowed for drop by drop feed. A minimal headspace was used to minimize volatilization of the TCE.

Equilibrium adsorption isotherms were determined for composite mixtures of each of the Chalmers and Russell soils for two different particle sizes, coarse (< 2 mm) and fine (< 0.150 mm). All adsorption isotherms were best described by the Freundlich theory with the following relationships: (1) Chalmers, fine: $X/M = 1.250C^{0.972}$; (2) Chalmers, coarse: $X/M = 0.813C^{0.949}$; (3) Russell, fine: $X/M = 0.826C^{0.910}$; (4) Russell, coarse: $X/M = 0.443C^{0.926}$ (X/M expressed in ug TCE adsorbed/g soil; C expressed as TCE equilibrium concentration in mg/l). These isotherms indicated the higher organic carbon content soil had the higher adsorptive capacity for TCE for both particle sizes tested. However, when normalized for the organic carbon content, the X/M indicated a dependence upon inorganic surface area adsorption.

TCE and soil adsorption equilibration time studies determined that adsorption equilibrium was reached within 15 hours for fine particle soil and within 20 hours for coarse particle soil. These studies were conducted for TCE concentrations of 220 and 880 mg/l for both soils. Glass and gravel adsorption studies indicated negligible adsorption. Based upon water application rates, the calculated residence

times of water within the columns (for both soils) were 30 days for 50 ml/day and 15 days for 100 ml/day. Soil column effluents were tested two to four times weekly for TCE concentration.

In all columns, TCE appeared in the effluent before one pore volume of water had been applied. This was believed to be due to both short-circuiting and TCE's specific gravity which is greater than that of water. The TCE concentrations in the effluents increased more rapidly for the low organic soil (Russell) than for the high organic soil (Chalmers) for both water application rates and TCE loadings used. The columns charged with 5 ml TCE showed a greater retardation of TCE through the column than did the columns charged with 10 ml TCE. This difference was less pronounced in the Russell soil than in the Chalmers soil.

Water application rates used in this study had no measurable effect on the elution of TCE from either type of soil or TCE loading studied. TCE concentration in the soil column effluents reached maximum values of 840-1,100 mg/l. TCE concentrations in Chalmers effluents were consistently lower than equivalent conditions for the Russell soil at the 5 ml TCE loading. For 10 ml TCE loadings, maximum concentrations for all columns rapidly reached and remained constant at approximately 1,100 mg/l, the maximum solubility of TCE. For this loading, the effluent TCE concentrations

from columns to which 100 ml/day of water was applied began to decrease after 5.3-5.9 pore volumes.

In only one column (Russell soil, 5 ml TCE, 50 ml water/day), was any free or undissolved TCE found in the effluent. Effluent from all other columns contained only TCE in solution as substantiated by dilution of samples before headspace analysis to quantify TCE. Comparison of actual TCE elution with theoretical TCE elution based upon TCE as a nonreactive substance indicated TCE was adsorbed and retarded in its movement through the soil. However, the continued water application eventually desorbed TCE with Russell soil showing greater TCE elution than the Chalmer's soil for similar conditions and total column effluent volume.

Column effluent pH was measured at approximately weekly intervals. For all columns, effluent pH was consistently greater than that of the water applied (pH 5.5-6.0). The mean pH for the columns ranged from 6.19-6.72. No difference in pH was noted for difference in soils, TCE loadings, or water application rates.

TCE biodegradation studies were conducted both in column elution and batch Warburg respirometric tests. To determine if nutrient addition would enhance biodegradation of TCE, water to one column of each column test group was supplemented with 10 mg/l ammonia nitrogen for days 75-100. During this period, measurement of effluent ammonia,

nitrate, chlorides, and TCE indicated no measurable enhancement of TCE degradation. Furthermore, nutrient addition showed no measurable depletion of ammonia nitrogen as evidenced by maximum effluent values of 8.0-12.0 mg/l of ammonia. Nitrate nitrogen levels in effluents of enhanced columns were approximately 0.5 mg/l higher than non-enhanced columns. Nitrite nitrogen was not detected in any of the column effluents.

Effluents from nutrient enhanced columns had mean chloride concentrations 2.0-6.0 mg/l higher than effluents from non-enhanced columns. This represented evidence of some form of degradation since degradation of TCE requires an initial dechlorination step that produces chloride ions. This increase in chloride concentration for the enhanced columns was not significant and the corresponding amount of TCE degradation it could represent was not measurably accounted for in the column effluents. Enhancement with ammonia was therefore discontinued due to its non-measurable effect on TCE degradation.

Concurrent with the column studies, aerobic biodegradation studies using Warburg respirometry were conducted. Initial respirometric studies used soil from a 2.5 inch depth of a Chalmers soil core which had not been used in column elution studies. TCE solutions ranging from 55-1,100 mg/l were used as test substrates with a glucose solution of

1,000 mg/l used as a biological activity indicator substrate. No oxygen uptake was measured for TCE while glucose showed evidence of oxygen uptake. All TCE solutions tested were inhibitory to biological activity as shown by oxygen uptakes that were less than control or endogenous uptakes. Further testing with acclimated soil showed oxygen uptake for .CE solutions of 55 mg/l but inhibition for 110 and 550 Biological degradation of TCE was greater for both mg/1. soils with samples at the 2.5 inch depth exhibiting greater degradation than samples from the 15 inch depth. Degradation was not demonstrated for either soil at the 31 inch Biodegradation was not considered to have been depth. inhibited by pH because the pH of the column effluents fell within the range for satisfactory biological growth.

As a measure of the validity of the Warburg test, the endogenous respiration and associated carbon dioxide productions were calculated for each soil and sample depth tested. Endogenous respiration rates ranged from 0.5-1.8 ul oxygen/g soil/hr with the corresponding carbon dioxide production of 24-83 ug carbon dioxide/g soil/day. These values compared favorably with the 5-50 ug carbon dioxide/g soil/day reported in the literature (1).

Abiotic degradation was evaluated by screening soil column effluents for cis-1,2-dichloroethylene and trans-1,

2-dichloroethylene. These compounds, the primary degradation products of TCE, were not detected in any of the column effluents at a minimum detection limit of 2 mg/l.

At the end of the column elution studies, soil samples, at various depths, were taken from one column of each column group. These samples were analyzed to determine the mass of TCE remaining on the soil. TCE soil concentrations were generally proportional to the organic carbon content of the sample depth. A comparison of the TCE remaining on the column with that predicted by the isotherms indicated the isotherms underestimated the TCE adsorptive capacity of the soil. Consequently, it was concluded that isotherms developed with aqueous solutions of TCE cannot accurately predict the adsorptive capacity and retardation of TCE applied to soil in a non-solution form.

Volatilization was calculated based upon the quantification of the fate of TCE from elution, degradation, and that remaining on the soil. The amount of TCE that eluted depended upon the total amount of water applied; however, elution was greater for the Russell soil than for the Chalmers soil at both TCE loadings and both water application rates. Degradation (both abiotic and biological) was calculated to have accounted for no more than 0.3% of the TCE applied to the columns. Volatilization, however, was calculated to account for 15.6-32.8% of the applied TCE despite the restrictive headspace used. Volatilization was

less from columns with water application rates of 100 ml/day than from those with 50 ml/day.

This research indicated that TCE spilled or discharged onto the soil in a non-solution form would neither be subject to immediate biological degradation nor would much degradation likely take place with time. Volatilization would be a likely route of major loss. The amount of TCE that would be eluted through the soil as a result of rainfall would not likely be affected by rainfall amounts. This was shown in these studies by the lack of effect of water application rates at equivalent rainfall rates of 0.43 and 0.86 inches/day.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From the research studies on the disposition and fate of TCE when applied to soil columns, the following conclusions could be drawn:

- 1. Adsorption isotherms developed in batch studies followed a Freundlich relationship for the soils and TCE concentration ranges tested.
- 2. Adsorption of TCE from solution in batch studies increased as the particle size of the soil decreased.
- 3. Adsorption of TCE from solution in batch studies was greater for the soil with the higher fraction of organic carbon.
- 4. Adsorption of TCE from solution in batch studies was due to both the organic carbon content and inorganic surface areas as shown in $K_{\rm OCF}$ of the soils tested.
- 5. Adsorption equilibrium between the TCE solutions (220 and 880 mg/l) and soil particles in batch studies was attained within 15 hours by the fine particle size (<0.150 mm) and within 20 hours by the coarse particle size soil (<2 mm) for both soils tested.

- 6. Adsorption of TCE onto glass and gravel surfaces was negligible at the concentration levels tested.
- 7. Adsorption and desorption of TCE for the soil within the columns was demonstrated.
- 8. Adsorption isotherms developed from batch studies with composite soil samples underestimated maximum adsorptive capacity for TCE directly applied to the column.
- 9. TCE eluted more rapidly from the soil with the lower fraction of organic carbon.
- 10. Elution was not affected by the rate of water application used.
- 11. Biological degradation of TCE within the soil columns was not measurably enhanced by application of ammonia nitrogen.
- 12. Aerobic biological degradation of TCE by unacclimated soils was not possible at TCE concentrations of 55-1,100 mg/l.
- 13. Aerobic biological degradation of TCE by acclimated spils was inhibited by TCE concentrations of 110 $\,\mathrm{mg/l}$ and higher.
- 14. Biological degradation of TCE was higher at 2.5 inch depth than at 15 inch depth for both soils.
- 15. Nutrient enhancement of aerobic degradation did not alter the rate of degradation but did increase the percentage of TCE respired at 55 mg/l.

- 16. Abiotic degradation of TCE within the soil columns was insignificant.
- 17. Degradation accounted for 0.3% or less of the TCE in the column studies.
- 18. Volatilization was a significant route of loss for TCE in the soil column studies and was calculated to range from 15.6-32.8%.

Recommendations for Future Research

This research focused on one particular chemical, TCE, and two representative soils in assessing the fate of a spill. This research did show that TCE would be eluted through the soil; however, other chemicals and other soil conditions are worth investigating.

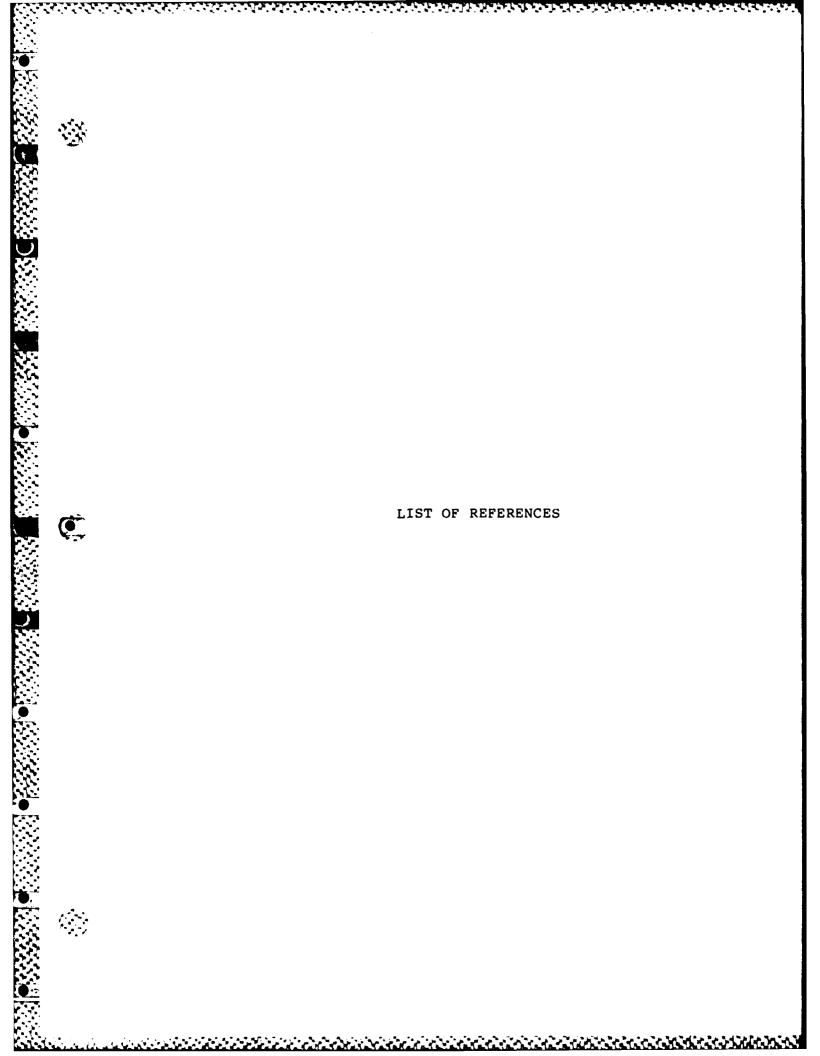
Additional research should be focused on the effects of ageing upon the desorptibility of an organic chemical from the soil. Varying the time of contact for a chemical upon the soil before elution is worth study.

Further studies should be conducted with cycles of water application followed by no water application to assess the effect of wetting/drying cycles upon the movement of TCE or other chemicals.

Volatilization was calculated to be a major route of loss in these investigations even though the columns contained a restrictive headspace. Comprehensive studies, tied in with wetting/drying cycles, could include actually capturing the volatilized chemical to quantify such losses.

Use of radiolabeled compounds would increase the ability to account for all forms of chemical fates.

Consideration should be given to bench scale or field tests wherein a quantity of chemical is applied to a soil, then the soil plowed or tilled to promote volatilization. Results could be quantified over time by actual extraction of soil samples.



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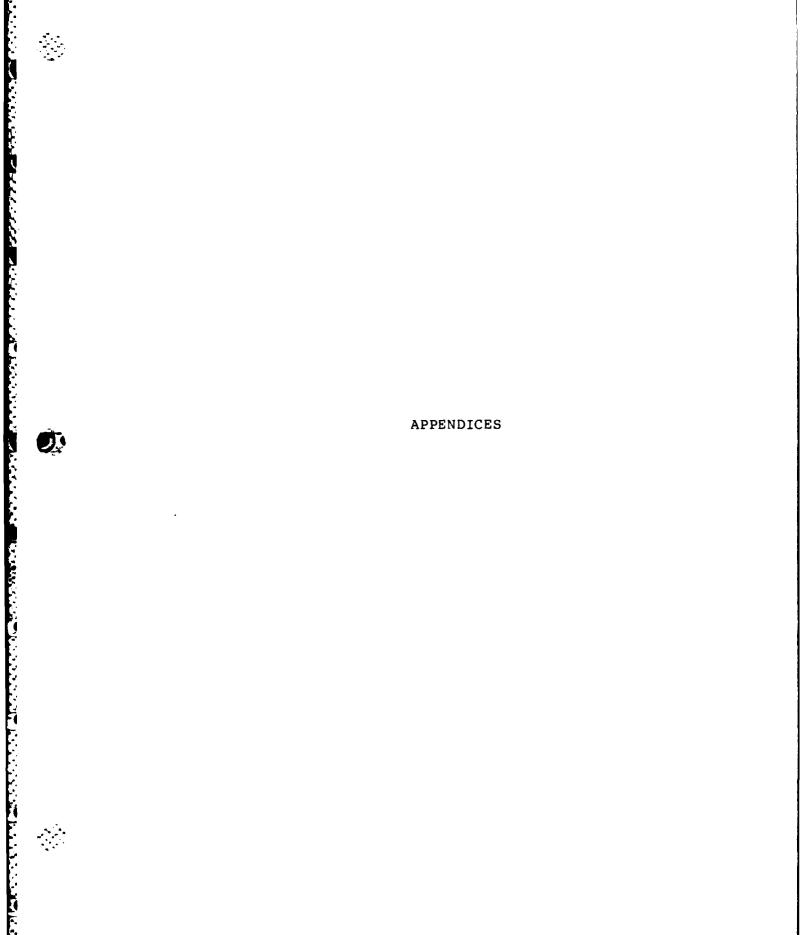
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Appendix A. Sample Calculations.

Sample Calculations

1. Porosity, n (unitless) (11).

$$n = 1 - BD \over \rho$$

where BD = Bulk Density, g/cm^3 ρ = Density of soil solids, g/cm^3

2. Bulk Volume, BV (cm³)

$$BV = H \times A$$

where H = Height of soil layer, cm A = Area of horizontal layer, cm² (A = 45.6 cm² for 3 inch diameter)

3. Pore Volume, PV (cm³).

$$PV = n \times BV$$

4. Soil Mass, SM (g).

$$SM = BD \times BV$$

5. Organic Carbon Mass, OCM (g).

$$OCM = SM \times f_{OC}$$

where f_{oc} = fraction of organic carbon

6. Total Bulk Density of Column, TBD (g/cm^3) .

$$TBD = \frac{SM (Total)}{BV (Total)}$$

7. Calculated Porosity of Column, nc (unitless).

Total % Organic Carbon, TPOC, %.

$$TPOC = \frac{Total \ OCM}{Total \ SM} \times 100$$

Mass of TCE remaining on soil after elution, g (grams).

$$g = (X/M)_e \times M_s$$

where $(X/M)_e = mg TCE/g soil (dry weight basis)$

determine from extraction

 M_s = Calculated mass of soil segment representative of extracted sample as indicated below:

Depth of Sample, in	Depth of Column Segment, in.	Ms, Chalmers	g Russell
2.5	0 - 8.25	1251.5	1312.5
15.0	8.25 - 24.75	2746	2864
30.0	24.75 - 33.00	1403	1482.5

Calcuated average soil water velocity, u (77).

$$u = \frac{QL}{PV}$$

where Q = Water application rate
 L = Length of soil column

PV = Pore Volume

11. Cumulative TCE eluted based upon CSTR (53).

$$\frac{-\text{CEV}}{\text{PV}}$$
% eluted = (1 - e) x 100%

where CEV = Cumulative Effluent Volume

PV = Pore Volume of Soil

Results listed in Table B18.

12. Theoretical COD of TCE.

$$2C_2HCl_3 + 4.5O_2 + 6e^- ----> 4CO_2 + H_2O + 6Cl^-$$

$$COD = \frac{(4.5 \text{ mole O}_2) (32 \text{ g/mole})}{(2 \text{ mole TCE}) (131.4 \text{g/mole})} = \frac{0.54 \text{ mg O}_2}{\text{mg TCE}}$$

13. Theoretical COD of Glucose.

$$c_6 H_{12} O_6 + 6 O_2 -----> 6 CO_2 + 6 H_2 O$$

$$COD = \frac{(6 \text{ mole O}_2) (32 \text{ g/mole})}{(1 \text{ mole glucose}) (180 \text{ g/mole})} = \frac{1.06 \text{ mg O}_2}{\text{mg glucose}}$$

Appendix B. Tabulated Data from Soil Column Studies.

Table Bl. Cross Reference of Column Study Day With Calendar Date.

Day	Date	Day	Date	Day	Date	Day	Date
A	4/3		oplied)			are for	1983.
0	4/4		Applic				
1 2	4/5	36	5/10	71	6/14	106	7/19
2	4/6	37	5/11	72	6/15	107	7/20
3	4/7	38	5/12	73	6/16	108	7/21
4	4/8	39	5/13	74	6/17	109	7/22
5	4/9	40	5/14	75	6/18	110	7/23
6	4/10	41	5/15	76	6/19	111	7/24
7	4/11	42	5/16	77	6/20	112	7/25
8	4/12	43	5/17	78	6/21	113	7/26
9	4/13	44	5/18	79	6/22	114	7/27
10	4/14	45	5/19	80	6/23	115	7/28
11	4/15	46	5/20	81	6/24	116	7/29
12	4/16	47	5/21	82	6/25	117	7/30
13	4/17	48	5/22	83	6/26	118	7/31
14	4/18	49	5/23	84	6/27	119	8/1
15	4/19	50	5/24	85	6/28	120	8/2
16	4/20	51	5/25	86	6/29	121	8/3
17	4/21	52	5/26	87	6/30	122	8/4
18	4/22	53	5/27	88	7/1	123	8/5
19	4/23	54	5/28	89	7/2	124	8/6
20	4/24	55	5/29	90	7/3	125	8/7
21	4/25	56	5/30	91	7/4	126	8/8
22	4/26	57	5/31	92	7/5	127	8/9
23	4/27	58	6/1	93	7/6	128	8/10
24	4/28	59	6/2	94	7/7	129	8/11
25	4/29	60	6/3	95	7/8	130	8/12
26	4/30	61	6/4	96	7/9	131	8/13
27	5/1	62	6/5	97	7/10	132	8/14
28	5/2	63	6/6	98	7/11		
29	5/3	64	6/7	99	7/12		
30	5/4	65	6/8	100	7/13		
31	5/5	66	6/9	101	7/14		
32	5/6	67	6/10	102	7/15		
33	5/7	68	6/11	103	7/16		
34	5/8	69	6/12	104	7/17		
35	5/9	70	6/13	105	7/18		

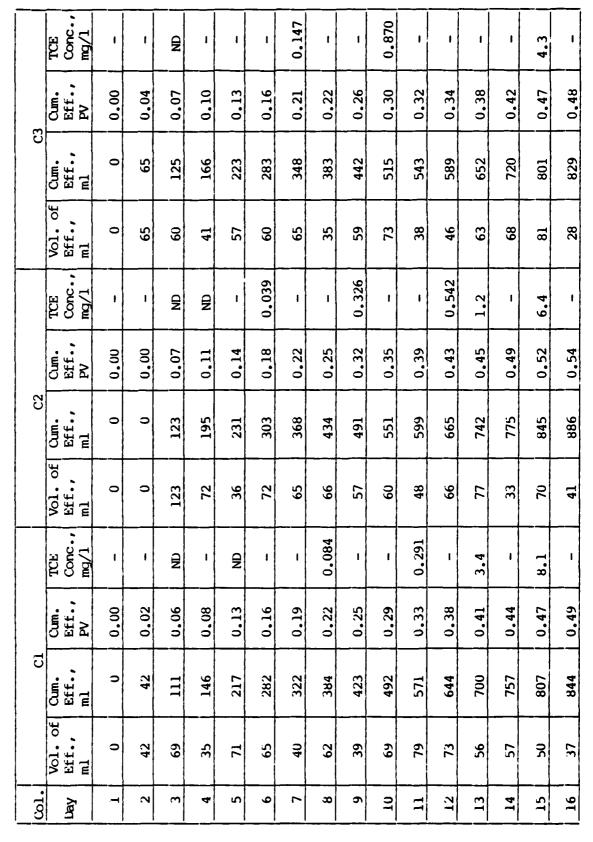


Table B2. Daily Data for Columns C1, C2, and C3.

Conc., mg/l 7.3 1.7 ı • ı ı ı Cum. Eff., PV 0.86 96.0 0.69 0.72 0.83 0.88 0.92 1.01 0.54 0.62 0.67 0.51 0.57 0.61 က Eff., ml S of Vol. c Eff., ml 6 4 Conc., TCE ı ı ı Cum. Eff., PV 0.54 0.57 0.59 0.62 0.64 0.68 0.72 0.75 0.79 0.83 0.87 0.91 0.93 96.0 1,00 1.04 Cum. Eff., ml Vol. of Eff., ml S တ္တ Conc., TCE ı ı Cum. Eff., PV d.53 0.70 0.88 0.58 0.64 0.72 0.75 0.79 0.83 0.85 0.95 96.0 0.60 0.67 1.01 0.91 U Eff., ml SEM. of Vol. C Erf., ml 8 Day

Table B2. Continued.

(e

TCE Conc., mg/1ŧ ı ı Oum. Eff., PV 1.18 1.26 1.29 1.32 1,35 1,38 1.43 1.46 1.50 1,03 1.07 1.41 1.21 Oum. Eff., ml of Vol. o Eff., ml TCE Conc., mg/1ı ı ı į ı ı Cum. Eff., PV 1.46 1,35 1.39 1.28 1.37 1.24 1.41 1.06 1.51 1,21 C_2 Cum. Eff. ml Vol. of Eff., ml TCE Conc., mg/l t ŧ ı Cum. Eff., PV 1.30 1.40 1.43 1.46 1.09 1.20 1.23 1.34 1.37 1.03 1.07 CCum. Eff., ml Vol. of Eff., I α ਤ Day

Table B2. Continued.

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Conc., mg/l 13E ı t Cum. Eff., PV 1,95 1.54 1.58 1.65 1.68 1.72 1.77 1.80 1.82 1.84 1.87 1.90 1.92 -1.61 က Eff., ml CLIM. Vol. of Eff., ml Conc., mg/l ı ł ı Cum. Eff., PV 1.66 1.70 1.73 1.76 1.83 1.90 1.96 1.98 2.04 1,55 1.62 1.80 1.87 1.93 2.01 1.58 Eff., ml Cum. Vol. of Eff., ml Conc., mg/1 ı Cum. Eff., PV 1,66 1.69 1.72 1.97 1.56 1.63 1.75 1.82 1.86 1.89 1.52 1.60 1.94 1.91 \Box Eff., ml C.m. Vol. of Eff., ml Day ረና

Table B2. Continued.

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Conc., mg/1 F ŧ ı Cum. Eff., PV 2.08 2.25 2.28 2.40 2.43 2.40 2.04 2.22 2.34 2.37 2.01 2.31 Cum. Eff., ml Vol. of Eff., ml TCE Conc., mg/1 ı ı ı ı Cum. Eff., PV 2.35 2.07 2.20 2.23 2.26 2.29 2,33 2.39 2.45 2.44 2.47 2.49 jo Vol. c Eff., ml Conc., mg/l ı ı ŧ ŧ ŧ Cum. Eff., FV 2.00 2.10 2.16 2.26 2.03 2.07 2.19 2,31 2,34 2.40 2.45 2.22 2.29 2.37 2.42 ರ Cum. Eft., ml Vol. of Eff., ml 9/ Day

Table B2. Continued.

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TCE Conc., mg/1ı ı ı t Cum. Eff., 2.90 2.93 2.49 2,55 2.58 2.76 2.84 2.52 2.64 2.67 2.87 2.61 2.81 Vol. of Eff., ml TCE Conc., mg/1 ŧ ı ı Cum. Eff., PV 2.90 2.96 2.52 2,55 2.79 2.82 2.85 2.87 2.93 2.58 2.64 2.67 2.61 Vol. of Eff., ml TCE Conc., ŧ ŧ t ı Cum. Eff., PV 5.66 2.69 2.75 2.48 2.89 2.92 2.54 2.57 2.60 2.63 2.72 2.84 2.87 2.51 2.81 \Box Vol. of Eff., ml . 19 Day

Table B2. Continued.

Conc., mg/1 ı 2.96 3.02 3.05 3,25 3,34 3,37 3.40 3.07 3.22 Vol. of Eff., ml Conc., ł ŧ 3.44 2.99 3.02 3.05 3.08 3.20 3.23 3.29 3,32 3,35 3.38 3.41 of Cum. Eff., PV 2.95 3.30 3,36 3,39 2.98 3.07 3.10 3.27 3.01 3.21 \Box Eff., ml Vol. of Ert., 2,5 . S bay

Table B2. Continued.

Conc., ı ı Cum. Eff., PV 3,43 3.49 3,55 3.60 3,63 3,66 3.84 3.52 3.57 3.69 3.87 3.81 Vol. of Eff., ml Conc., mg/1TCE. ı Cum. Eff., PV 3.47 3,53 3.56 3.58 3.64 3.67 3.73 3.82 3,85 3.88 3,91 3.50 3.61 Vol. of Eff., I Conc., ı ı ŧ ı Cum. Eff., PV 3.60 3.63 3.65 3.68 3,83 3.86 3.54 3.77 3.80 3.57 3,51 \Box Eff., ml Vol. of Eff., ml . 193 Day

Table B2. Continued.

C3
Vol. of Cum. C3
Eff., Eff., Eff., Conc., mq/1
51 6663 3.90 52 6715 3.93 49 6764 3.96 451
47 6811 3.98 -Vol. of Eff., ml TCE Conc., mg/l 4.35 382 ı 1 Eff., PV Cum. 3.94 3.96 3.99 4.02 Cum. Eff., ml 6730 6780 6828 6880 Vol. of Eff., ml 48 50 52 51 TCE Conc., mg/l 511 1 ı 1 Cum. Err., PV 3.89 3,97 3.92 3.94 CICum. Eff., 6645 9699 6743 6792 Vol. of Ett., ml 46 49 5 47 col. Day 129 130 131 132

Table B2. Continued.

Conc., mg/112 142 TCE Θ ı 9 1 ŧ 1 (ı 1 Cum. Eff., PV 0.00 0.08 0.20 0,35 0.42 0.47 0.62 0.69 0.95 1.00 0.01 0.27 0.52 0.88 0.77 Eff., ml 273 345 0 12 137 460 602 712 899 C. 802 1059 1186 1713 1324 1499 1627 of Vol. c Eff., ml 136 0 125 115 12 72 110 142 160 138 128 8 97 127 175 98 Conc., 0.087 0.464 mg/1 $\frac{1}{2}$ ١ ١ ١ i 38 28 82 Cum. Eff., PV 0.00 0.09 0.16 0.23 0.04 0.28 0.35 0.48 0.76 0.54 0.62 0.86 0.41 0.82 0.93 0.71 Eff., ml \supset 65 153 280 969 1066 1296 601 821 931 1208 1399 1480 1594 391 Vol. of Etf., ml 0 88 127 88 122 95 125 110 135 142 65 88 103 81 Conc., mg/l 0.068 0.228 3.9 ł Θ 2 ı 1 ı ١ ı 53 Cum. Eff., PV 0.15 0.10 00.0 0.26 0.39 0.22 0.32 0.44 0.49 0.62 0.69 0.01 0.54 0.82 0.87 Cum. Etf., ml) 170 255 546 744 833 923 1176 23 451 661 1054 1284 1397 1488 of Etf., ml Vol. 147 118 115 0 23 85 78 સ 83 3 122 108 131 86 7 Sol. ~ S ထ Day 4 9 7 Ŋ 70 13 14 15 91

Table B3. Daily Data for Columns C4, C5, and C6.

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Conc., mg/1ı ı ı ı Cum. Eff., PV 1,30 1,45 1.50 1,55 1.60 1.82 1.89 1.04 1,09 1,23 1,67 C. Vol. of Eff., ml TCE Conc., mg/1ı ŧ ı Cum. Eff., PV 1.48 1.80 1.00 1.03 1.22 1,37 1,43 1.57 1.64 1.70 1.27 1,51 Vol. of Eff., ml Conc., mg/1ı ı ı ı ı t Cum. Eff., PV 1.30 1,35 1,75 96.0 1.07 1.12 1.19 1.25 1.44 1.64 1.69 0.92 1,01 1.57 1.51 C4Vol. ot Eff., ml . 19 Day

Table B3. Continued.

Table B3. Continued.

	TCE Conc., mg/1	ı	793	1	ı	761	-	803	_	812	1	836	ı	851	ı	1	ı
	Cum. Eff., PV	1.94	1.99	2.04	2.09	2.15	2.22	2.28	2.34	2.40	2,46	2.52	2.56	2.60	2.66	2.71	2.76
90	Cum. Eff., ml	3325	3408	3487	3574	3680	3793	3900	3994	4110	4215	4300	4371	4454	4548	4635	4725
	Vol. of Eff., ml	94	83	79	87	106	113	107	94	116	105	85	7.1	83	94	87	90
	TCE Conc., mg/l	-	618	1	1	808	ı	860	ı	897	l	912	1	873	1	881	i
	Cum. Eff., PV	1.87	1,94	2.00	2.07	2.14	2.21	2.28	2.33	2.39	2.44	2.49	2.53	2,58	2.63	2.69	2.74
CS	Cum. Eff., ml	3204	3313	3427	3533	3651	3777	3891	3987	4080	4164	4251	4327	4419	4499	4595	4685
	Vol. of Eff., ml	117	109	114	106	118	126	114	96	93	84	87	76	92	80	96	06
	TCE Conc., mg/l	•	705	1	í	730	1	716	1	754	1	840	I	922	ł	931	ł
	Cum. Eff., PV	1.84	1.89	1.95	2.02	2.08	2,15	2.21	2.27	2,33	2.40	2.46	2.52	2.57	2.62	2.67	2.72
C4	Cum. Eff., ml	3189	3239	3332	3440	3553	3670	3781	3884	3981	4095	4204	4301	4389	4471	4562	4649
	Vol. of Etf., ml	131	50	93	114	107	11.7	111	103	76	114	109	76	88	82	91	97
[3]	Day	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48

Conc., ı ı t ŧ t Oum. Eff., PV 3.66 3.49 2.82 2.98 3.03 3.25 3.37 3,55 2.87 2.92 3.07 3.61 3,31 S. of Vol. Conc., mg/l 9/8 TCE Oum. Eff., PV 3,30 3,43 3.49 3,55 3.60 2.89 2.98 3.03 3,14 3.24 2.84 2.94 Oum. Eff., ml Vol. of Eff., ml Conc., ŧ • Cum. Eff., PV 30.09 3.46 2.85 2.97 3.03 3.20 3.25 3.29 3,34 3.40 3.56 3.62 2.91 3,51 S. Vol. of Eff., ml Lay 6

Table B3. Continued.

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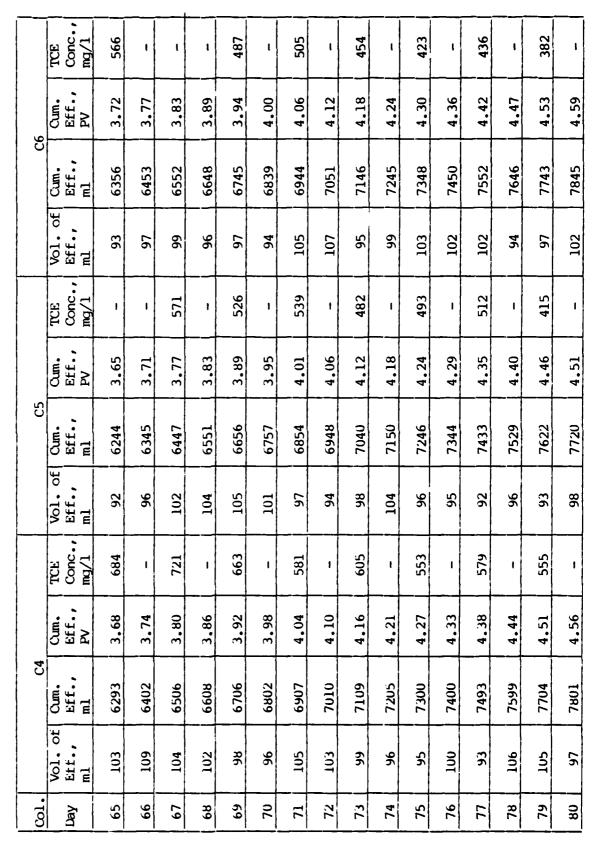


Table B3. Continued.

TCE Conc., mg/1 . Cum. Eff., PV 5.06 5,53 4.65 4.83 4.89 4.95 5.00 5.23 5.30 5,35 5.41 5.47 of TCE Conc., mg/14.76 5.05 5.22 5,39 5,45 4.82 4.88 5.00 4.58 4.64 5.11 5.27 S. Eff., Vol. of Eff., ml TCE Conc., $\frac{m}{\sqrt{2}}$ ı ı ţ Cum. Eff., PV 4.62 4.68 4.85 4.98 5.09 5.15 5,20 5.26 5,32 5,38 5.44 5.50 4.92 Vol. of Eff., ક્ર Sol. Lay ጟ

Table B3. Continued.

Table B3. Continued.

Etf., of Cum. Cum. Cum. TCE TOTC. VOI. of Cum. Cum. Cum. TCE TOTC. VOI. of Cum. Cum. TCE TOTC. Cum. TCE TOTC.	601.	1 1	C4				CS				90	1 1	
97 9508 5.56 302 101 9417 5.51 244 96 9604 5.62 - 97 9514 5.56 - 94 9608 5.67 314 96 9610 5.62 248 99 9797 5.73 - 102 9712 5.68 - 103 9900 5.79 303 98 9810 5.79 - 104 10,106 5.91 306 99 10,000 5.86 - 104 10,106 5.91 306 99 10,000 5.85 183 104 10,204 5.97 - 99 10,101 5.91 - 9 96 10,300 6.08 - 97 10,291 6.08 201 103 10,390 6.08 - 97 10,291 6.14 - 99 10,694 6.25 193 10,693 <t< th=""><th>Day</th><th>Vol. of Eff., ml</th><th>Cum. Eff., ml</th><th>Cum. Eff., PV</th><th>• </th><th>Vol. of Eff., ml</th><th>Cum. Eff., ml</th><th>Cum. Eff., PV</th><th>•</th><th>Vol. of Eff., ml</th><th>Cum. Eff., ml</th><th>Cum. Eff., PV</th><th>TCE Conc., mg/l</th></t<>	Day	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	•	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	•	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
96 9604 5.62 - 97 9514 5.56 - 94 9698 5.67 314 96 9610 5.62 248 99 9797 5.73 - 102 9712 5.68 - 103 9900 5.79 303 98 9810 5.74 229 102 10,002 5.85 - 99 9909 5.74 229 104 10,106 5.91 306 99 10,000 5.85 183 104 10,106 5.91 306 99 10,000 5.85 183 98 10,204 5.97 - 93 10,104 5.91 - 90 10,300 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,502 6.14 - 99 10,790 6.25 193 10,1699 6.26	76	76	9508	5.56	302	101	9417	5,51	244	86	9547	5.58	263
94 9698 5.67 314 96 9610 5.62 248 99 9797 5.73 - 102 9712 5.68 - 103 9900 5.79 - 102 9712 5.68 - 102 10,002 5.85 - 99 9909 5.79 - 104 10,106 5.91 306 99 10,000 5.85 183 98 10,204 5.97 - 93 10,101 5.91 - 96 10,300 6.02 263 93 10,194 5.96 201 103 10,390 6.08 - 97 10,291 6.02 - 102 10,493 6.14 254 10,199 6.08 - 10 102 10,595 6.20 - 107 10,502 6.14 - 99 10,790 6.31 - 96 10,699	86	95	9604	5.62	-	97	9514	5.56	ı	103	9650	5.64	-
99 9797 5,73 - 102 9712 5.68 - 103 9900 5,79 303 98 9810 5,74 229 102 10,002 5,85 - 99 9909 5,79 - 104 10,106 5,91 306 99 10,000 5,85 183 98 10,204 5,97 - 93 10,101 5,91 - 96 10,300 6,02 263 93 10,194 5,96 201 103 10,390 6,08 - 97 10,291 6,02 - 103 10,493 6,14 254 104 10,395 6,08 212 99 10,794 6,25 193 101 10,699 6,26 - 96 10,790 6,31 - 96 10,699 6,26 - 100 10,890 6,37 222 98 10,797 <td>99</td> <td>94</td> <td>8696</td> <td>5.67</td> <td>314</td> <td>96</td> <td>9610</td> <td>5,62</td> <td>248</td> <td>100</td> <td>9750</td> <td>5,70</td> <td>271</td>	99	94	8696	5.67	314	96	9610	5,62	248	100	9750	5,70	271
103 9900 5.79 303 98 9810 5.74 229 102 10,002 5.85 - 99 9909 5.79 - 104 10,106 5.91 306 99 10,000 5.85 183 98 10,204 5.97 - 93 10,194 5.91 - 96 10,300 6.02 263 93 10,194 5.96 201 90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 - 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,699 6.26 - 100 10,890 6.37 - 96 10,699 6.26 - 105 10,995 6.43 - 99 10,896 </td <td>100</td> <td>66</td> <td>9797</td> <td>5,73</td> <td>-</td> <td>102</td> <td>9712</td> <td>5.68</td> <td>_</td> <td>100</td> <td>9850</td> <td>5.76</td> <td>'</td>	100	66	9797	5,73	-	102	9712	5.68	_	100	9850	5.76	'
102 10,002 5.85 - 99 9909 5.79 - 104 10,106 5.91 306 99 10,000 5.85 183 98 10,204 5.97 - 93 10,101 5.91 - 96 10,300 6.02 263 93 10,194 5.96 201 90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 10,10,699 6.26 - 100 10,890 6.31 - 96 10,699 6.26 - 105 10,995 6.43 - 99 10,896 6.37 -	101	103	0066	5.79	303	86	9810	5.74	229	105	9955	5.82	228
104 10,106 5.91 306 99 10,000 5.85 183 98 10,204 5.97 - 93 10,101 5.91 - 96 10,300 6.02 263 93 10,194 5.96 201 90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,699 6.26 - 100 10,790 6.31 - 96 10,699 6.26 - 100 10,995 6.43 - 99 10,896 6.37 -	102	102	10,002	5.85	١	66	6066	5.79	1	86	10,053	5,88	-
98 10,204 5,97 - 93 10,101 5.91 - 96 10,300 6.02 263 93 10,194 5.96 201 90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,603 6.26 - 100 10,890 6.31 - 96 10,699 6.26 - 105 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	103	104	10,106	5.91	306	96	10,000	5.85	183	102	10,155	5.94	212
96 10,300 6.02 263 93 10,194 5.96 201 90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,699 6.26 - 100 10,890 6.31 - 96 10,699 6.26 - 105 10,995 6.43 - 99 10,896 6.37 -	104	85	10,204	5.97	ı	93	10, 101	5.91	ı	101	10,256	9.00	ı
90 10,390 6.08 - 97 10,291 6.02 - 103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,699 6.26 - 96 10,790 6.31 - 96 10,699 6.26 - 100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	105	96	10,300	6.02	263	93	10,194	5.96	201	104	10,360	90.9	192
103 10,493 6.14 254 104 10,395 6.08 212 102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,603 6.20 184 96 10,790 6.31 - 96 10,699 6.26 - 100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	106	96	10,390	6.08	1	76	10,291	6.02	1	102	10,462	6.12	-
102 10,595 6.20 - 107 10,502 6.14 - 99 10,694 6.25 193 101 10,603 6.20 184 96 10,790 6.31 - 96 10,699 6.26 - 100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	107	103	10,493	6.14	254	104	10,395	90.9	212	66	10,561	6.18	209
99 10,694 6.25 193 101 10,603 6.20 184 96 10,790 6.31 - 96 10,699 6.26 - 100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	108	102	10,595	6.20	ı	107	10,502	6.14	ı	76	10,658	6.23	1
96 10,790 6.31 - 96 10,699 6.26 - 100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	109	66	10,694	6.25	193	101	10,603	6.20	184	85	10,756	6.29	232
100 10,890 6.37 222 98 10,797 6.31 - 105 10,995 6.43 - 99 10,896 6.37 -	110	96	10,790	6.31	1	96	10,699	6.26	1	100	10,856	6,35	
105 10,995 6.43 - 99 10,896 6.37 -	111	100	10,890	6.37	222	86	10,797	6.31	1	105	10,961	6.41	179
	112	105	10,995	6.43	1	66	10,896	6.37	1	101	11,062	6.47	1

TCE Conc., mg/l 147 183 109 103 167 159 ŧ 1 ı ŧ • 1 1 Cum. Eff., PV 6.53 6.59 6.54 6.82 6.88 6.94 7.05 7.22 Eff., ml 11,164 12,153 12,452 12,555 12,057 11,860 12,251 11,263 11,361 11,557 11,658 11,758 11,958 12,351 Cum. of Vol. c Eff., ml 100 103 102 86 102 98 66 96 86 98 100 9 9 101 97 101 TCE Conc., mg/l 106 139 172 152 142 189 161 i ı 1 1 ı Cum. Eff., PV 5.43 6.49 6,55 6.79 6.85 96.9 7.08 7.25 6.67 6.90 7.02 7,31 6,61 S 12,030 12,404 Cum. Eff., ml 504 11,209 11,310 11,705 11,905 12,007 12,206 10,999 11,103 11,510 12,110 11,807 11,411 11,607 12, of Vol. C Eff., ml 103 104 106 102 102 103 100 101 101 96 101 97 98 8 97 TCE Conc., mg/l 198 202 183 123 103 187 167 231 1 ı ı t Cum. Eff., PV 6.72 6.95 7.36 6.49 6.55 99.9 6.78 7.24 6.84 6.90 7.07 7.30 6,61 7,01 11,987 Eff., ml 11,098 11,199 11,396 11,597 11,888 12,190 12,286 12,490 12,588 11,497 11,694 11,792 12,088 12,387 11,297 CLE. of Etf., ml 103 101 102 103 8 101 32 3 100 97 35 96 3 101 8 25 3 Day 115 116 118 119 120 123 124 125 126 127 128 117 122 121

Table B3. Continued.



Q.

	TCE Conc. mg/1	83	ı	98	ı							
	Cum. Eff., PV	7.46	7.52	7.58	7.63							
90	Cum. Eff., ml	12,751	12,852	12,954	13,050							
	Vol. of Eff., ml	76	101	102	96							
	TCE Conc., mg/l	112	-	128	ı							
	Cum. Eff., PV	7.37	7.43	7.49	7.54							
35	Cum. Eff., ml	12,601	12,703	12,801	12,843							
	Vol. of Eff., ml	97	102	86	92							
	TCE Conc., mg/l	108	ı	ı	ı							
	Cum. Eff., PV	7.42	7.47	7.53	7.59		!					
C4	Cum. Eff., ml	12,685	12,779	12,877	12,978							
	Vol. of Eff., ml		94	86	101				i			
8	Гау	129	130	131	132							

Table B3. Continued.

Conc., 0.076 mg/1 $\frac{2}{8}$ 2.7 ı ı ı ı 1 15 ı ı ı ı Cum. Eff., PV 0.10 0.25 0.28 0.40 0.43 0.46 0.00 0.08 0.13 0.22 0.33 0.35 0.37 0.48 0.04 Eff., ml 172 228 385 592 989 729 784 825 0 140 307 560 627 62 471 431 Vol. of Eff., 0 79 46 32 59 43 62 78 32 56 78 40 83 35 55 41 Conc., 0.146 mg/11.6 12.8 8.2 i 2 ١ 1 1 17 f ١ \exists Cum. Eff., PV 0.40 0.00 0.00 0.05 60.0 0.12 0.19 0.22 0.27 0.35 0.44 0.47 0.50 0.53 0.31 Eff., CEM. 203 242 319 455 528 969 8/9 862 0 0 89 160 384 747 799 901 Vol. of Eff., 0 0 89 43 39 65 73 89 69 52 63 39 11 7 82 71 Conc., 0.122 0.672 mg/12 ī ŧ 3.2 8.6 1 2 ı ŧ Eff., 0.00 0.05 0.12 0.16 0.18 0.22 0.30 0.35 0.39 0.43 0.52 0.08 0.27 0.47 0.50 Ckm, 0.01 ≥ C_{2} Eff., Cum. 0 12 79 144 200 273 312 383 456 664 736 797 855 521 891 E Vol. of Ett., ml \supset 12 65 99 73 39 73 85 58 36 **67** 71 65 19 58 9 ~ 9 16 S _ သ IJ 10 Ţ 17 13 14 15 Day

Table B4. Daily Data for Columns C7, C8, and C9.

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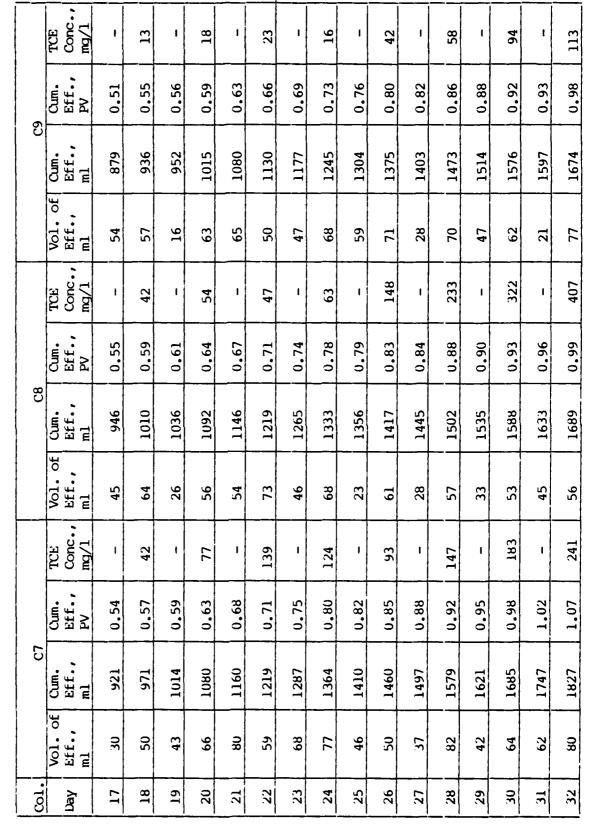


Table B4. Continued.

Conc., t ı ŧ ι ŧ l l t Cum. Eff., PV 1.22 1.25 1.35 1.47 1.00 1.44 1.04 1.08 1.31 1.41 Cum. Eff., ml of Vol. c Eff., ml TCE Conc., mg/l l ι ι ı ι Cum. Eff., PV 1.08 1.24 1.26 1.30 1,33 1.36 1,38 1.40 1.44 1.47 1.04 1.01 1.21 ဆ Cum. Eff., ml of Vol. o Eff., ml TCE Conc., mg/l 1. ı ı Į l t Cum. Eff., PV 1.42 1.56 1.34 1.46 1.53 1.08 1.20 1.27 1.31 1.37 1.50 C_{J} Cum. Eff., ml of Vol. c Eff., ml 4 501. 4] Day

Table B4. Continued.

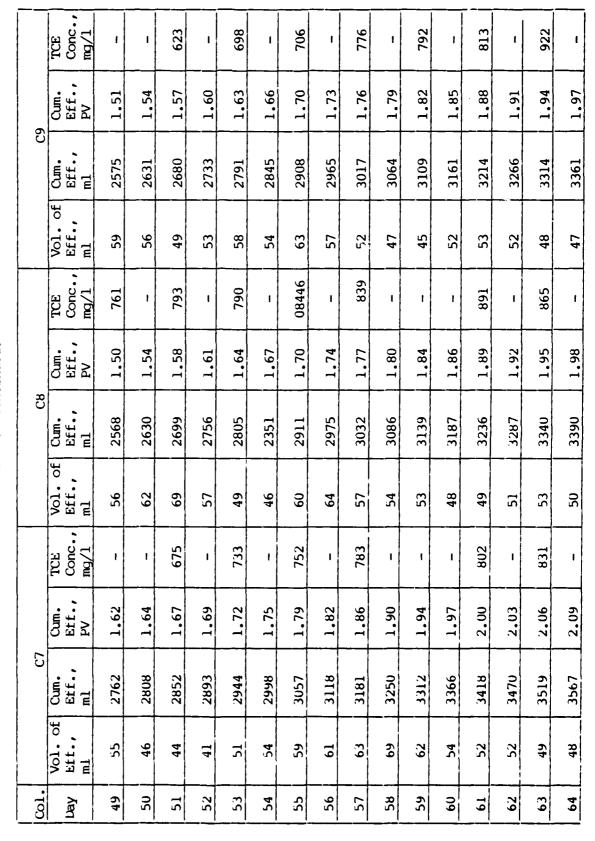
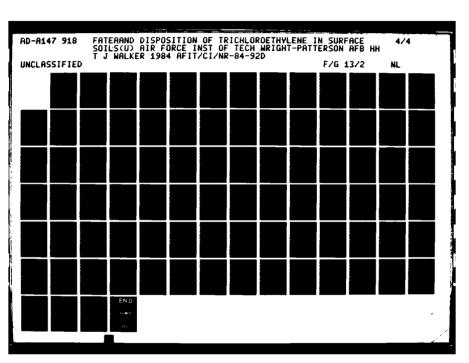
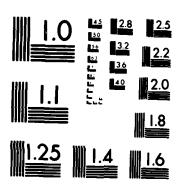


Table B4. Continued.





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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

	TCE Conc., mg/l	1	-	863	1	868		938	•	963		1	-	941	1	1	
65	Cum. Eff., PV	1.99	2.02	2.05	2.08	2.11	2.14	2.17	2.20	2.23	2.26	2.29	2.32	2,35	2.37	2.40	
	Cum. Eff., ml	3405	3454	3507	3558	3605	3658	3713	3767	3820	3872	3917	3963	4011	4058	4107	
	Vol. of Eff., ml	44	49	53	51	47	53	55	54	53	52	45	46	48	47	49	
	TCE Conc., mg/l	884	1	928	1	939	ı	I	1	1024	I	1018	1	1036	_	1062	
	Cum. Eff., PV	2.01	2.04	2.07	2.10	2.13	2.16	2.19	2.22	2,25	2.28	2.31	2.34	2.36	2.40	2,43	
83	Cum. Eff., ml	3442	3489	3535	3583	3635	3688	3743	3794	3844	3896	3947	3993	4042	4098	4152	
	Vol. of Eff., ml	52	47	46	48	52	53	55	51	50	52	51	46	49	56	54	
	TCE Conc., mg/l	826	1	888	-	ι	ı	931	1	806	•	954	ı	943	1	980	
	Cum. Eff., PV	2.12	2.15	2.18	2.21	2.23	2.26	2.29	2.32	2,35	2.38	2.41	2.44	2.46	2.49	2.52	
7.2	Cum. Eff., ml	3617	3671	3727	3774	3819	3865	3913	3960	4012	4065	4114	4164	4212	4263	4310	
	Vol. of Ett., ml	50	54	- 56	47	45	46	48	47	52	53	49	50	48	51	47	
501.	Lay	\$	99	67	89	69	70	71	72	73	74	75	76	77	78	79	

Table B4. Continued.

gers/Espains and property (Espains) appropried to the second of the seco

Table B4. Continued.

Col.		C7				C8				60		
Day	Vol. of Etf., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc.,
81	50	4413	2.58	-	53	4261	2.49	i	51	4209	2.46	994
82	49	4462	2.61	1	48	4309	2.52	!	52	4261	2.49	ı
83	54	4516	2.64	987	54	4363	2.55	1127	51	4312	2.52	1008
84	52	4568	2.67	1	51	4414	2.58	ı	46	4358	2,55	ı
85	51	4619	2.70	776	47	4461	2.61	1068	48	4406	2,58	966
98	54	4673	2.73	1	48	4509	2.64	ŧ	47	4453	2.60	ı
87	51	4724	2.76	1027	52	4561	2.67	1041	49	4502	2.63	965
88	50	4774	2.79	1	49	4610	2.70	ı	51	4553	2.66	ı
83	49	4823	2.82	1040	51	4661	2.73	1060	53	4606	2.69	988
3	48	4871	2.85	ı	47	4708	2.75	ı	52	4658	2.72	ı
16	48	4919	2.88	1010	50	4758	2.78	1	55	4713	2.76	1044
92	47	4966	2.90	1	49	4807	2.81	1	53	4766	2.79	1
73	52	5018	2.93	1080	51	4858	2.84	1010	53	4819	2.82	1023
94	51	5069	2.96	ı	53	4911	2.87	ı	51	4870	2,85	ı
35	53	5122	3.00	ı	52	4963	2.90	1037	47	4917	2.88	1072
96	54	5176	3.03	1	51	5014	2.93	ı	49	4966	2.90	1

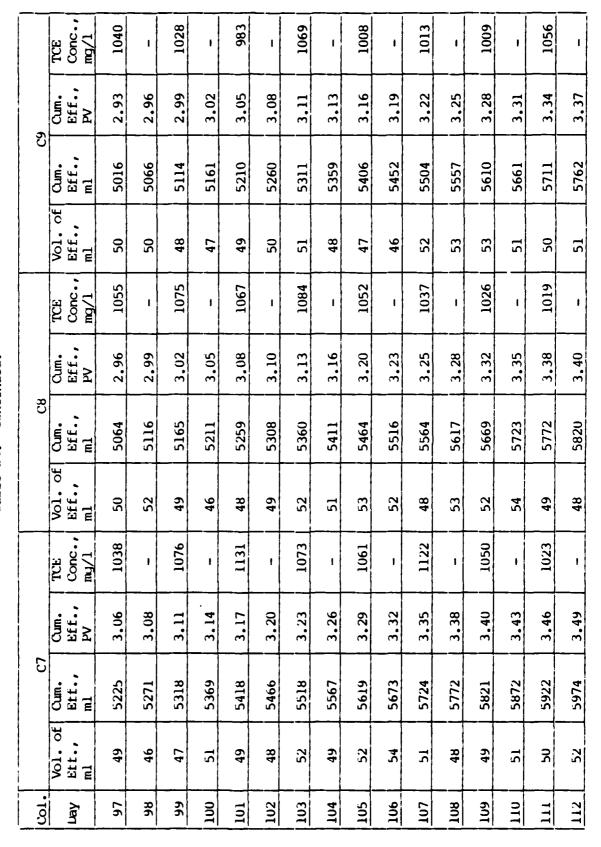


Table B4. Continued.



D.

	TCE Conc., mg/1	1053	ı	987	ı						
	Cum. Eff., PV	3.86	3.89	3.92	3,95						
	Cum. Eff., ml		9599	6707	6757						
	Vol. of Eff., ml	52	52	51	50						
	TCE Conc., mg/1	1053	1	1035	-						
	Cum. Eff., PV	3.90	3,93	3.96	3,99						
83	Oum. Eff., ml	6672	6717	07.19	6824						
	Vol. of Eff., ml	46	45	53	54						
	TCE Conc., mg/1										
	Cum. Eff., PV										
C7	Cum. Eff., ml										
	Vol. of Etf., ml										
Co1.	Day	129	130	131	132					-	

Table B4. Continued.

Conc., mg/1ZE ı 2 ı 168 ı g ı ı 14 1 ω 8 ı Cum. Eff., PV 0.00 0.02 0.11 0.17 0.24 0.29 0.36 0.40 0.47 0.56 0.52 0.62 99.0 0.70 0.78 0.85 C12 Eff., ml Cum. 0 43 183 288 494 9/9 883 611 811 996 1060 1133 1330 1450 1201 of Vol. c Eff., ml 0 43 140 105 123 83 117 135 65 83 94 73 89 129 120 Conc., 0.392 0.167 3.7 ı \mathbf{g} 23 ı 92 41 1 Table B5. Daily Data for Columns C10, Cum. Eff., PV 0.372 0.00 0.05 0.12 0.19 0.24 0.30 0.44 0.50 0.50 0.56 0.63 0.72 0.67 0.78 0.81 c11Eff., ml S 0 87 202 324 418 507 848 6307 8480 965 757 1149 1070 1233 1340 1391 of Eff., ml 0 115 87 122 94 33 123 127 9 117 105 91 79 107 84 51 Conc., $m_J/1$ 2.8 1 ı $\frac{2}{2}$ 173 Θ ı ı ı 72 ı t Cum. Eff., PV 00.0 0.02 0.10 0.14 0.43 0.29 0.36 0.21 0.48 0.53 0.58 0.64 0.78 0.71 0.85 0.92 C10 Eff., ml Ę S 0 174 234 358 41 494 618 743 830 903 1103 992 1221 1328 1460 1573 Vol. of Eff., ml) 130 41 63 136 124 125 124 73 8 111 118 113 87 107 132 3 Day m 4 2 و ဆ 37 2 12 15 16 1 13 14

Daily Data for Columns C10, C11, and C12.

Table B5. Continued.

Co1.		C10	0			C11	1			Ö	C12	
Гау	Vol. of Eff., ml	Cum. Ett., ml	Cum. Eff., PV	TCE Conc., my/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
17	96	1669	0.98	801	74	1465	0.86	1	91	1541	06.0	1
18	76	1745	1.02	328	136	1601	0.94	290	107	1648	96.0	387
19	18	1826	1.07	ı	91	1692	0.99	1	09	1708	1.00	•
70	89	1894	1.11	392	68	1781	1.04	352	59	1767	1.03	502
21	115	2009	1.18	,	90	1871	1.09	1	94	1861	1.09	1
22	93	2102	1.23	588	98	1957	1.14	515	76	1937	1.13	449
23	98	2188	1.28	-	77	2034	1.19	ı	83	2020	1.18	1
24	106	2.294	1.34	543	108	2142	1.25	524	91	2111	1.24	452
25	129	2423	1.42	,	85	2227	1.30	1	88	2199	1.29	-
26	116	2539	1.48	594	06	1217	1.36	618	123	2322	1.36	672
27	122	2661	1.56	-	79	2396	1.40	ı	96	2418	1.41	•
28	133	2794	1.64	662	115	2511	1.47	730	81	2499	1.46	889
29	114	2908	1.70	١	126	2637	1.54	1	116	2615	1.53	
30	85	2990	1.75	788	85	2722	1.59	748	119	2734	1.60	704
31	19	3051	1.78	,	93	2815	1.65	•	142	2876	1.68	1
32	126	3177	1.86	835	130	2945	1.72	637	133	3009	1.76	697

Conc., mg/1ι ı Eff., PV 2.78 1,83 1.98 2.04 2,10 2.20 2.32 2,38 2.45 2.52 2.59 2.65 2.72 Cum. 1.91 C12 Eff., Cum. Vol. of Eff., TCE Conc., mg/1ı ı t Cum. Eff., PV 2.08 2.65 1.79 1.98 2.04 2.20 2.26 2.35 2.47 2.54 2.59 1.86 1.93 2,31 c11Vol. of Eff., TCE Conc., mg/1ı ı ı service, broken) Cum. Eff., PV 2.50 2.06 2,23 2.36 2.43 2.56 1.96 2.29 1.91 2.01 (Taken out of Vol. of Etf., ml Day

Table B5. Continued.

3		T W	49	50	51	52	53	54	55	99	57	58	59	09	19	62	63	64
	E T	Ē																_
	1 -	₹															-	
	TCE Conc.,	mg/1												-				
	Vol. of Eff.,	m]	87	83	94	91	87	94	104	112	103	101	96	86	95	91	94	95
	<u> </u>	m]	4612	4695	4789	4880	4967	5061	5165	5277	5380	5481	5577	5675	5770	5861	5955	0509
	· I	P	2.70	2.75	2.80	2.85	2.90	2.96	3.02	3.09	3, 15	3.21	3,26	3.32	3,37	3.37	3.48	3 54
	TCE Conc.,	mg/1	1012	1	992	1	,	,	1013	,	984	1	1021	,	955	J	982	
	Vol. of Eff.,	m]	86	92	901	112	103	16	85	83	87	93	86	94	92	96	68	8
	Cum. Eff.,	m	4857	4949	5055	5167	5270	5361	5446	5527	2614	5707	5805	5899	5991	6081	6170	6563
	C12 Cum. Eff.,	75	2.84	2.89	2.96	3.02	3.08	3.14	3.18	3 23	2 20	3.34	3,39	3.45	3, 70	3.56	3.61	10.0
	TCE	mg/1	1038	ı	1003		,	•	1017	1	200	7.01	966	1		ı	920	3

Table B5. Continued.

Eff., PV 3.72 3.77 3,83 3.89 3,95 4.01 4.07 4.30 4.36 4.42 4.60 Vol. of Eff., ml Conc., mg/l ı ŧ ı ı Cum. Eff., PV 3,59 3,65 3.83 3.88 3.71 3.94 4.00 4.05 4.17 4.30 4.23 4.42 4.47 4.11 Eff., ml Cum. Vol. of Eff., ml TCE Conc., mg/l Cum. Eff., PV Cum. Eff., ml Vol. of Etf., ml . 103 Day 3 9/

Table B5. Continued.

(

Table B5. Continued.

	of G	C10 Cum.	1 1	TCE	Vol. of	C1]	·i	TCE	Vol. of	1 1	C12 Cum.	TŒ.
Etf.,	a) EF	Eff., ml	BEE., Ps.	Conc., mg/l	Eff., ml	Eff., ml	Eff., PV	Conc., mg/l	Eff., ml	Eff., ml	Eff., PV	Conc., mg/1
					66	7749	4.53	€96	102	7965	4.66	981
					102	7851	4.59	1	103	9808	4.72	•
1					86	7949	4.65	901	86	8166	4.78	896
- 1					95	8044	4.70	ı	86	8263	4.83	1
1					66	8143	4.76	1022	66	8362	4.89	983
					103	8246	4.82	1	96	8458	4.95	-
					66	8345	4.88	1016	95	8553	2.00	1027
					100	8445	4.94	_	94	8647	90*5	1
- 1					95	8540	4.99	686	94	8741	5.11	1003
	-				92	8632	5.05	ı	76	8838	5.17	e.
1					66	8731	5.11	1041	97	8935	5.23	1071
1	_				103	8834	5.17	ı	66	9034	5.28	ı
- 1					103	8937	5,23	992	104	9138	5,34	1
- 1					105	9042	5.29	1	102	9240	5.40	ı
- 1	_				97	9139	5.34	973	104	9344	5.46	991
1		-			96	9235	5.40	ı	103	9447	5.52	1

ı

Cum. Eff., PV 5,59 5.76 6.05 6.17 6.35 6.46 5.65 5.82 5.88 5.94 6.00 6.22 6.29 6.41 6.11 5.71 C12 10,546 10,748 10,644 10,851 11,055 10,253 10,447 10,954 10,054 10,151 10,351 9552 9658 9756 9850 9953 of Vol. c Eff., ml 105 106 102 86 103 101 86 96 96 86 104 103 103 101 94 97 TCE Conc., mg/l 907 952 937 912 897 811 789 692 ı t ı ı 1 Cum. Eff., PV 5.46 5.63 5.69 5.74 5.80 5.86 5.92 60.9 6.15 5.52 5.57 5.97 6.03 6.27 6.32 6.21 CII 10,116 Cum. Eff., ml 10,522 10,211 10,421 10,719 10,815 10,017 10,314 10,622 9819 9330 9530 9624 9722 9921 Vol. of Eff., ml 86 95 96 95 102 97 102 96 99 103 107 100 76 94 101 TCE Conc., mg/l Cum. Eff., C10 Cum. Eff., ml Vol. of Etf., ml 3 Day 102 103 105 106 110 112 7 86 66 100 101 104 107 **308** 109 111

Continued. Table B5.

Conc.

mg/1

952

894

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873

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882

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840

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863

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692

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		010				110						
Lay	vol. of Ett.,	H. H	1 -	TCE Conc.,	Vol. of Eff.,	Cum. Eff.,	I	TCE Conc.,	Vol. of Eff.,	Cum. Eff.,	1	TCE Conc.,
	E E	m]	Σ	mg/1	[m]	m]	ΡV	mg/l	m]	THE	&	mg/1
113					86	10,913	6,38	733	104	11,159	6.53	653
114					101	11,914	6.44	0	102	11,261	6.59	1
115					101	11,115	6.50	029	86	11,359	6.64	583
116					102	11,217	95.9	ı	101	11,460	6.70	
117					95	11,312	6.62	682	97	11,557	6.76	588
118					86	11,410	6.67	ł	66	11,656	6.82	t
119					66	11,509	6.73	627	100	11,756	6.87	535
120					101	11,610	6.79	1	100	11,856	6.93	-
121					86	11,708	6.85	612	98	11,954	6.99	490
122					103	11,811	6.91	ı	96	12,050	7.05	1
123					104	11,915	6.97	543	66	12,149	7.10	486
124					102	12,017	7.03	ı	101	12,250	7.16	ı
125					101	12,118	7.09	558	102	12,352	7.22	403
971					100	12,218	7.15	ı	97	12,449	7.28	ı
127					66	12,317	7.20	541	102	12,551	7.34	407
128					100	12,417	7.26	ı	102	12,653	7.40	1

Table B5. Continued.

Table B5. Continued.

	TCE Conc., mg/l	322	1	371	1							
C12	Cum. Eff., PV	7.46	7.52	7.57	7.63							
[]	Cum. Eff., ml	12,751	12,851	12,950	13,043							
	Vol. of Eff., ml	86	100	66	93	 						
	TCE Conc., mg/1	508	1	429	ı							
	Cum. Eff., PV	7.32	7.37	7.43	7.49							
C11	Cum. Eff., ml	12,512	12,608	12,706	12,808							
	Vol. of Eff., ml	55	96	85	102							
	TCE Conc., mg/l						_					
	Cum. Eff., PV											
C10	Cum. Eff., ml											
	Vol. of Eft., ml								•			
Col.	Day	129	130	131	132							

Table B6. Daily Effluent Volume from Chalmers Soil Control Column.

1	Effluent		Effluent		Effluent
Day	Collected, m	Day	Collected, ml	Day	Collected, ml
1	0	24	118	47	111
2	127	25	75	48	102
3	*133	26	133	49	109
4	109	27	86	50	116
5	125	28	96	51	122
6	136	29	67	52	108
7	82	30	85	53	96
8	73	31	113	54	89
9	91	32	89	55	83
10	142	33	75	56	91
11	*83	34	86	57	95
12	116	35	79	58	101
13	108	36	88	59	105
14	85	37	99	60	107
15	*141	38	114	61	103
16	80	39	121	62	109
17	93	40	118	63	101
18	112	41	106	64	*97
19	126	42	122	65	93
20	130	43	136	66	94
21	108	44	*127	67	91
22	110	45	113	68	96
23 *Ind	127	46	118 for TCE analysi	69	99

*Indicates sample taken for TCE analysis. No TCE detected in any samples.

Table B6. Continued.

. ———	· · · · · · · · · · · · · · · · · · ·				
	Effluent		Effluent		Effluent
Day	Collected, m	l Day_	Collected, ml	Day	Collected, ml
70	95	93	*96	116	96
71	102	94	95	117	99
72	103	95	92	118	103
73	102	96	97	119	*101
74	98	97	98	120	98
75	97	98	101	121	103
76	93	99	100	122	101
77	*96	100	97	123	98
78	97	101	96	124	97
79	96	102	99	125	99
80	101	103	97	126	98
81	103	104	102	127	100
82	100	105	*103	128	102
83	107	106	101	129	104
84	96	107	*104	130	101
85	98	108	97	131	93
86	97	. 109	103	132	104
87	96	110	102		
88	99	111	102		
89	101	112	101		
90	107	113	99		
91	102	114	102		
92 *Ind	98 icates sample	115 taken	100 for TCE analys:	is. No	TCE detected

*Indicates sample taken for TCE analysis. No TCE detected in any samples.

0.698 Conc., 0.624 ₽ ₽ £ 2 mg/11 ı 1 Cum. Eff., PV 0.00 0.05 0.08 0.20 0.33 0.36 0.40 0.44 0.48 0.56 0.22 0.24 0.27 52 ં Eff., CLIM. 438 0 192 324 356 585 704 130 530 901 25 391 of Vol. o Eff., ml 0 55 62 75 55 62 42 8 32 35 47 92 59 ල 7 64 TCE Conc., 0.892 0.289 mg/1 ₹ 2 28 19 1 ı 5 Cum. Eff., 0.00 0.15 0.20 0.25 0.28 0.32 0.35 0.39 0.43 0.46 0.58 0.02 0.54 0.07 0.11 0.51 **R**2 Cum. Eff., ml 325 936 176 247 455 568 830 872 0 35 107 631 751 Vol. of Eff., ml 0 35 78 46 25 63 53 79 64 28 69 7 84 **67** 4.2 TCE Conc., 0.742 0.146 28 mg/1 $\frac{2}{3}$ 13.8 ı ı ı t t ŧ Į 1 0.46 0.42 0.00 90.0 0.10 0.15 0.19 0.22 0.24 0.29 0.33 0.37 0.40 0.52 0.56 09.0 \mathbb{Z} Eff., ml Cum.) 165 247 312 349 394 466 529 685 752 899 92 601 841 651 971 Vol. of Eff., 0 73 73 82 69 37 45 63 3 34 89 28 E ٥ σ 10 3 Lay ~ S x 12 14 15 16

Table B7. Daily Data for Columns R1, R2, and R3.

•



	TCE Conc., mg/l	'	ı	3.1-	'	19	ı	12	ı	31	ı	99	١	123	ı	231	ı
	Cum. Eff., PV	0.50	09.0	0.65	0.67	0.70	0.73	0.77	0.80	0.83	0.85	0.89	0.91	96.0	0.97	1.00	1.03
R3	Cum. Eff., ml	934	975	1052	1082	1138	1177	1243	1290	1351	1382	1443	1481	1550	1577	1627	1671
	Vol. of Eff., ml	33	41	77	30	26	39	99	47	61	31	61	88	69	72	50	44
	TCE Conc., mg/l	-	'	41	-	9/	J	97		186	ı	257	•	368	ı	402	-
	Oum. Eff., PV	09.0	0.62	0.65	0,67	0.71	0.73	0.76	0.81	0.85	0.90	0.93	0.97	1.02	1.04	1.08	1,10
R2	Cum. Eff., ml	972	966	1056	1087	1151	1178	1237	1305	1378	1458	1512	1575	1646	1680	1746	1782
	Vol. of Eff., ml	36	24	09	31	64	27	59	89	73	980	54	63	7.1	34	99	36
	TCE Conc., mg/l	,	-	67	'	53	ı	71	ı	96	ı	148	1	192	1	218	-
	Cum. Eff., PV	0.62	0.63	69*0	0.73	0.76	0.79	0.82	0.85	0.89	0.91	0.94	0.97	1.01	1.02	1.07	1.08
R	Cum. Eff., ml	1006	1023	1124	1183	1233	1273	1335	1379	1445	1481	1531	1572	1629	1660	1727	1756
	Vol. of Eff., ml	34	17	101	- 65	20	40	63	43	99	36	50	41	57	31	67	29
601.	Day	17	18	19	70	77	22	23	24	25	56	27	78	29	30	31	32

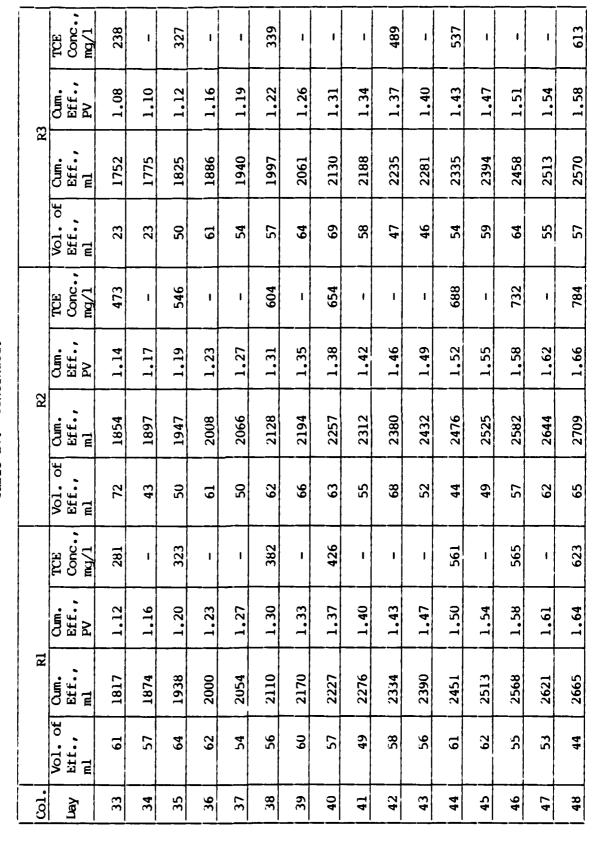


Table B7. Continued.



Table B7. Continued.

	TCE Conc., mg/l	1	712	1	694	1	718	1	883	1	865	ı	912	ı	1	-	936
	Oum. Eff., PV	19.1	1.65	1.69	1.73	1.77	1.82	1.86	1,91	1,95	1,99	2.03	2.06	2.09	2.12	2,15	2,18
R3	Cum. Eff., ml	2622	2676	2734	2801	2872	2944	3018	3094	3164	3228	3291	3345	3393	3437	3483	3530
	Vol. of Eff., ml	52	54	- 85	29	71	72	74	76	70	64	63	54	48	44	46	47
	TCE Conc., mg/l	1	802	-	1	ı	838	ı	845	ı	831	ı	794	,	810	ı	1
	Cum. Eff., PV	1.70	1.75	1.79	1.83	1.87	1.90	1.93	1.97	2.00	2.04	2.06	2.10	2.13	2.16	2,19	2.22
R2	Cum. Eff., ml	2772	2837	2905	2967	3025	3077	3133	3192	3247	3298	3345	3395	3448	3499	3547	3596
	Vol. of Eff., ml	63	65	89	62	- 85	52	56	59	55	51	47	20	53	51	48	49
	TCE Conc., mg/l	-	1	1	677	-	992	,	744	1	758	'	ı	'	843	1	880
	Cum. Eff., PV	1,66	1.69	1.72	1.76	1.80	1.84	1.88	16.1	1.94	1,98	2.01	2.04	2.07	2,10	2.13	2.16
RI	Cum. Eff., ml	2701	2740	2789	2845	2908	2975	3039	3096	3150	3201	3254	3309	3361	3410	3410	3504
	Vol. of Eft., ml	36	39	49	26	63	- 29	49	57	54	51	23	55	5.5	52	49	84
- log	Гау	49	20	51	52	53	54	55	56	57	28	65	09	19	62	63	49

Conc., mg/l ı 1.1 ŧ ı ı Cum. Eff., PV 2.24 2.27 2.30 2.33 2.37 3,43 2.46 2.49 2.52 2.55 2.50 2,62 2.65 2.68 2.21 CLEM. of Vol. c Eff., ml TCE Conc., mg/l ı ı t Oum. Eff., PV 2.25 2.40 2.43 2.46 2.49 2.55 2.70 2.31 2.37 2.52 2.58 2.64 2.67 2.61 \mathbf{Z} Cum. Eff., Vol. of Eff., TUE Conc., mg/l ı ı Cum. Eff., 2.38 2.22 2.25 2.28 2.44 2.50 2.65 2.47 2,53 2,55 2.59 2.62 2.31 2.41 \mathbf{z} Ett., Vol. of Eff., \$ 2,5 <u>ල</u> 5 Za E

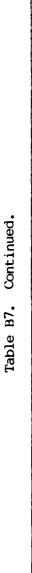
Table B7. Continued.

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Conc., ı t Oum. Eff., PV 2.80 2.87 2.90 2.93 2.96 2.99 3.04 3.08 2.71 2.77 2.84 3.01 3.11 Vol. of Conc., mq/1ZE Oum. Eff., PV 3,19 2.73 2.76 2.86 2.89 2.92 2.98 3,10 3,13 2.79 2.83 2.95 3.04 3.07 3.01 Cum. Eff., 3.07 Vol. of TCE Conc., mg/1ı Cum. Eff., PV 2.84 2.90 3,14 2.68 2.74 2.96 2.99 3.02 3.08 2.87 2.94 3.05 2.71 2.81 Z Eff., S. Vol. of Eff., Lay

Table B7. Continued.

C.



∞1.		Rl				R2				83		
Day	Vol. of Eff., ml	Cum. Eff., ml	Oum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
76	50	5137	3.17	_	52	5218	3.22	1	51	5194	3.21	'
86	52	5189	3.20	1004	48	5266	3.25	1069	49	5243	3.24	1074
66	51	5240	3,23	-	46	5312	3.28	ı	47	5290	3.27	1
001	20	5290	3.27	981	45	5357	3.31	1019	48	5338	3.30	1039
101	51	5341	3,30	•	48	5405	3.34	•	49	5387	3.33	ı
102	49	5390	3,33	866	49	5454	3.37	1010	53	5440	3.36	1047
103	53	5443	3.35	ı	52	5506	3.40	1	52	5492	3,39	ı
104	51	5474	3,38	907	51	5557	3.43	1024	50	5542	3.42	1117
105	53	5547	3.42	ı	51	5608	3.46	•	53	5595	3,45	1
106	54	5601	3.46	841	52	2660	3.49	958	46	5641	3,48	686
107	51	5652	3.49	1	51	5711	3,53	1	51	5692	3,51	-
108	50	5702	3.52	872	47	5758	3,55	947	49	5741	3,54	943
109	50	5752	3,55	1	49	5807	3.58	'	48	5789	3,57	•
011	47	5799	3.58	883	48	5855	3.61	892	51	5840	3.60	890
111	48	5847	3.61	-	51	5906	3,65	1	52	5892	3.64	'
711	64	9689	3.64		52	5958	3.68	852	53	5945	3.67	912



Vol.		[Z]	E	T.	Vol	R2		J. L.	Vol	R3	3	- J
or cum. Eff., ml	Etf., ml	3 2 ₹		Conc., mg/l	•	Eff., ml	Eff., PV	Conc.,	•	Eff., ml	Eff., PV	Conc.,
47 5943 3.67		3.6	57	ı	51	6009	3.71	1	51	2996	3.70	1
52 5995 3.70		3.7	9	820	49	6058	3.74	772	49	6045	3.73	855
51 6046 3.73		3.7	3	ı	48	9019	3.77	ı	47	6092	3.76	1
51 6097 3.76		3.7	9	804	51	6157	3.80	739	51	6143	3.79	-
50 6147 3.79	\dashv	3.75		'	52	6209	3.83	•	50	6193	3.82	•
51 6198 3.83		3.83		ı	51	6260	3.86	1	51	6244	3.85	762
48 6246 3.86		3.86		1	47	6307	3.89	•	50	6294	3.89	1
53 6299 3.89		3.89		797	52	6359	3.93	758	49	6343	3.92	781
52 6351 3,92		3.92		١	48	6407	3,95	١	52	6395	3.95	1
49 6400 3.95		3,95		683	49	6456	3,99	745	51	6446	3.98	029
48 6448 3.98		3.98		ı	51	6507	4.02	ı	48	6494	4.01	1
50 6498 4.01	- 	4.0		-	50	6557	4.05		49	6543	4.04	682
51 6549 4.04		4.0		ı	52	6099	4.08	ı	47	6590	4.07	•
48 6597 4.07		4.0		632	49	6658	4.11	682	51	6641	4.10	718
50 6647 4.10		4.1	0	1	48	9029	4.14		50	1699	4.13	-
49 6696 4.13		4.1	3	610	51	6757	4.17	752	49	6740	4.16	651

Table B7. Continued.

	TCE Conc., mg/l	1	623	,	١								
1	Cum. Eff., PV	4.19	4.22	4.25	4.28								
R3	Cum. Eff., ml	6792	6842	6892	6940			-					
	Vol. of Eff., ml	52	20	50	48								_
	TCE Conc., mg/l	ı	ı	ı	763								_
	Cum. Eff., PV	4.20	4.23	4.26	4.29								
R2	Cum. Eff., ml	6809	6857	6904	6955								
	Vol. of Eff., ml	52	48	47	51								
	TCE Conc., mg/l	ı	1	•	586					·			
	Cum. Eff., PV	4.17	4.20	4.23	4.26								
R	Cum. Eff., ml	6749	6801	6854	6903		İ						
	Vol. of Eff., ml	53	52	53	49								
81.	Гву	129	130	131	132								





	R6	1. of Cum. Cum. TCE E., Eff., Eff., Conc., ml PV mg/l	- 00°0 0 0	- 94 0.06 -	9 213 0.13 -	334 0.20 ND	5 420 0,26 -	530 0,32 0,623	2 622 0.38 -	5 747 0.46 -	9 866 0.53 -	955 0.59 3.9	3 1048 0.64 -	1132 0.69 -	5 1208 0.74 -	1279 0,78 43	7 1376 0.84 -	
		TCE Vol. Conc., Eff. mg/l ml		- 94	- 119	ND 121	98 -	- 110	0.583 92	- 125	3.7 119	- 8	- 93	44 84	92 -	94 71	- 87	
		Cum. Eff., PV	0.00	0.04	0.11	0.17	0.24	0.33	0.40	0.44	0.47	0.52	0.59	99.0	0.72	0.78	0.85	
	R5	Cum. Eff., ml	0	71	183	270	392	530	652	715	765	838	963	1069	1159	1256	1371	
•		Vol. of Eff., ml	0	71	112	87	122	138	122	63	50	73	125	106	90	97	115	
		TCE Conc., mg/l	ı	Q.	1	-	2	ı	'	0.542	ı	ı	1,5	ı	1	26	1	
		Oum. Eff., PV	0.00	90.0	0.12	0.17	0.21	0.26	0.34	0.40	0.46	0.52	0.57	0.65	0.74	08.0	98.0	
	R4	Cum. Eff., ml	0	106	196	269	339	414	557	644	753	838	930	1056	1194	1301	1397	
		Vol. of Etf., ml	Э	106	06	73	0,2	75	143	87	109	85	92	126	138	107	96	
	CO1.	Кeп		7	٣	4	S	9	7	ω	ی	21	11	12	13	14	15	

R6 Cum. Eff., ml Vol. of Eff., ml TCE Conc., mg/l Oum. Eff., PV 0.95 1.00 **R**5 Eff., ml Cum. Vol. of Eff., ml Conc., Eff., PV 0.99 1.06 Cum. **R**4 Eff., ml S.

Continued.

Table B8.

Conc., mg/l ı ı ı ı Cum. Eff., PV 1.02 1.69 1.82 1.09 1.29 1.40 1.52 0.97 1,25 1,34 1.47 1,57 1.64 1.21 7 ł 1.04 1.08 1.42 1,63 1.83 1.29 1.37 1,57 1.67 ı ı ı 1.27 1.34 1.48 1,57 1.63 1.69 1.87 1.93 1.21 1.41 1.81 Vol. of Eff., ml 7 Day

Conc., ı ı ı ı Cum. Eff., PV 2.56 2.02 2.28 2.40 2.45 2.50 2.66 1.96 2.08 2.13 2.23 2.61 1.87 1,90 **R6** Vol. of Eff., TCE Conc., mg/1ı Cum. Eff., PV 2.06 2.25 2.30 2,36 2.46 2.52 2.63 2.68 2.73 2.57 1,91 1.97 2.01 2.41 Vol. of Eff., TCE Conc., 2,30 2.36 2.59 2.75 2.96 2.02 2.06 2.23 2.44 2.68 2.82 2.89 1.97 2.51 Vol. of Eff., ml 9/ Day

Table B8. Continued.

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801.		L				R5	i L			R6		
Day	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc.,	Vol. of Eff., ml	Cum. Eff., ml	Com. Eff., PV	TCE Conc., mg/l
49	96	4920	3.02	1	94	4538	2.78	١	90	4426	2.72	1
20	94	5014	3,10	982	106	4644	2.87	١	93	4519	2.79	1053
51	90	5104	3.15	1	110	4754	2.93	ı	85	4604	2.84	-
52	92	5196	3.21	1	111	4865	3.00	922	16	4695	2.90	868
53	84	5280	3.26		114	4979	3.07	1	96	4791	2.96	-
54	86	5366	3,31	176	118	5097	3.15	937	107	4898	3.02	912
55	91	5457	3,37	ı	109	5206	3.21	•	112	5010	3.09	ı
26	103	5560	3.43	961	97	5303	3.27	877	117	5127	3.16	ı
57	105	5995	3.50	ı	102	5405	3.34	1	108	5235	3.23	ı
28	106	1773	3.56	979	104	5509	3.40	849	106	5341	3,30	951
59	102	5873	3.63	•	100	5609	3.46	-	103	5444	3,36	ı
09	95	5968	3.68	921	96	5705	3.52	863	94	5538	3.42	1038
19	06	8509	3.74	ı	93	5798	3.58	ı	91	5629	3.47	ı
62	94	6152	3.80	952	94	5892	3.64	1	99	5728	3.54	983
63	96	6248	3.86	ı	97	5989	3.70	1	96	5824	3.60	1
64	103	6351	3.92	906	95	6084	3.76	803	106	5930	3.66	948

Table B8. Continued.

Table B8. Continued.

]		9		<u>س</u>		6				8		9		2		8 0
	TCE Conc., mg/l	1	906	_ '	873		769	'	823	'	778		636		622		518
9	Cum. Eff., PV	3.73	3.79	3.85	3.92	3.98	4.04	4.10	4.16	4.21	4.27	4.34	4.40	4.46	4.52	4.58	4.64
R6	Cum. Eff., ml	6039	6143	6245	6343	6440	6541	6638	6733	6825	6923	7025	7124	7224	7320	7418	7519
	Vol. of Eff., ml	109	104	102	86	97	101	97	95	92	86	102	66	100	96	98	101
	TCE Conc., mg/l	-	1	ı	817	1	773	'	722	1	712	1	576	ţ	548	ı	909
	Cum. Eff., PV	3.82	3.88	3,95	4.01	4.08	4.14	4.21	4.27	4.34	4.40	4.46	4.52	4.58	4.64	4.71	4.77
R5	Cum. Eff., ml	6186	6292	6395	6499	8099	6713	6820	6925	7028	7131	7231	7328	7422	7520	7624	7277
	Vol. of Eff., ml	102	106	103	104	109	105	107	105	103	103	100	97	94	86	104	103
	TCE Conc., mg/l	1	933	ı	,	1	862	ι	827	,	678	,	627	ı	288	,	453
	Cum. Eff., PV	3.98	4.05	4.11	4.17	4.23	4.29	4.35	4.41	4.47	4.53	4.59	4.66	4.72	4.78	4.84	4.90
R4	Cum. Eff., ml	6452	9559	6662	6763	6858	6949	7044	7142	7238	7338	7440	7546	7650	7747	7842	7940
:	Vol. of Eff., ml	101	104	106	101	95	16	95	86	96	100	102	106	104	76	95	86
801.	Гау	65	99	29	89	69	20	7.1	72	73	74	75	76	77	78	79	98

Table B8. Continued.

103		R4				R5				R6		
Гау	Vol. of Etf., ml	Oum. Eff., ml	Oum. Eff., PV	TCE Conc., mg/1	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
81	96	8036	4.96	-	105	7832	4.83	-	97	7616	4.70	-
87	66	8135	5.02	402	66	7931	4.90	392	103	7719	4.76	453
83	103	8238	5.09	ı	96	8027	4.95	1	104	7823	4.83	_
84	104	8342	5,15	412	86	8125	5.02	374	97	7920	4.89	427
85	102	8444	5.21	-	97	8222	5.08	1	96	8016	4.95	1
98	66	8543	5.27	305	96	8318	5.13	339	95	8111	5.01	449
87	96	8639	5,33	ı	95	8413	5.19		94	8205	5.06	1
88	102	8741	5.40	220	66	8512	5.25	327	97	8302	5.12	395
68	96	8837	5,45	ı	102	8614	5.32	ı	103	8405	5.19	
96	95	8932	5,51	203	101	8715	5,38	358	101	8506	5.25	386
91	97	9029	5.57	١	86	8813	5.44	•	96	8602	5,31	•
92	96	9125	5.63	227	100	8913	5.50	308	86	8700	5.37	1
93	86	9223	5.69	1	101	9014	5.56	•	102	8802	5,43	ı
94	101	9324	5.76	212	103	9117	5.63	273	66	8901	5.49	338
95	103	9427	5.82	1	66	9216	5.69	1	96	8997	5,55	1
96	105	9532	5.88	218	95	9311	5.75	179	95	9092	5.61	264



Q.

	TCE Conc., mg/l	1	247	ı	249	I	223	•	202	ı	180	t	187	1	189	1	163
۰,6	Oum. Eff., PV	5.67	5.73	5.80	5.85	5.91	5.97	6.03	60.9	6.16	6.22	6.29	6,35	6.41	6.47	6.54	6.60
R6	Cum. Eff., ml	9193	9290	9390	9483	9577	6296	9775	9873	9266	10080	10183	10284	10383	10489	10592	10694
	Vol. of Eff., ml	101	97	100	93	94	102	96	86	103	104	103	101	66	901	103	102
	TCE Conc., mg/l	,	•	•	164	!	151	t	135	1	124	1	139	,	146	I	84
	Cum. Eff., PV	5.81	5.87	5.93	00*9	90•9	6,12	6.18	6.24	6.30	6.36	6.43	6.49	6,55	6.61	6.67	6.74
R5	Cum. Eff., ml	9408	9507	9611	9713	9816	9919	10017	10113	10211	10311	10412	10509	10604	10702	10806	10911
	Vol. of Eff., ml	97	66	104	102	103	103	86	96	86	100	101	97	95	86	104	105
	TCE Conc., mg/l	-	189	,	212	ı	174	ı	147	1	139	ı	102	1	123	,	110
	Cum. Eff., PV	5,95	6.01	6.07	6.13	6.19	6.25	6.32	6.38	6.44	6.50	6.56	6.62	69.9	6.75	6.81	6.88
R4	Cum. Eff., ml	9636	9739	9836	9930	10028	10129	10232	10333	10436	10532	10631	10730	10835	10939	11039	11140
	Vol. of Ett., ml	104	103	76	94	86	101	103	101	103	95	66	66	105	104	100	101
∞1.	Day	97	86	66	100	101	102	103	104	105	106	107	108	109	110	111	1112

Table B8. Continued.

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Col.		R4				85				R6		
Ьау	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
113	100	11240	6.94	_	102	11013	6.80	-	100	10794	99*9	-
114	99	11339	7.00	75	95	11108	98.9	87	101	10895	6.73	154
115	76	11436	7.06	1	66	11207	6.92	1	66	10994	6.79	ı
116	98	11534	7.12	79	103	11310	86.9	93	100	11094	6.85	147
117	97	11631	7.18	1	100	11470	7.04	•	97	11191	6.91	
118	101	11732	7.24	112	66	11509	7.10	104	86	11289	6.97	185
119	102	11834	7.30	ı	102	11611	7.17	1	97	11386	7.03	1
120	100	11934	7.37	1	97	11708	7.23	96	103	11489	7.09	124
121	99	12033	7.43	1	96	11804	7.29	•	104	11593	7,16	1
122	101	12134	7.49	97	66	11903	7.35	78	101	11694	7.22	127
123	66	12233	7.55	'	101	12004	7.41	ı	94	11788	7.28	•
124	97	12330	7.61	84	95	12099	7.47	139	103	11891	7.34	92
125	100	12430	79.7	١	86	12197	7,53	1	101	11992	7.40	1
126	101	12531	7.74	63	86	12295	7.59	84	94	12086	7.46	67
127	98	12629	7.80	ı	102	12397	7.65	ı	76	12183	7.52	1
128	76	12726	7.86	74	66	12496	7.71	89	66	12282	7.58	1

Continued.	
පි	
B8.	
Table	

	TCE Conc., mg/l	١	48	ı	75							
	Cum. Eff., PV	7.64	7.70	7.76	7.83							
R6	Cum. Eff., ml	12377	12477	12579	12682							
	Vol. of Eff., ml	95	100	102	103							
	TCE Conc., mg/l	'	72	-	38				_	-		
	Cum. Eff., PV	7.7	7.84	7.90	7.95							
R5	Cum. Eff., ml	12589	12695	12792	12881							
	Vol. of Eff., ml	93	106	97	68						 -	
	TCE Conc., mg/l	'	52	-	1							
	Cum. Eff., PV	7.92	7.98	8.04	8.11							
R4	Cum. Eff., ml	12826	12930	13031	13131							
	Vol. of Eff., ml	100	104	101	100							
C01.	Day	129	130	131	132	-						



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Conc., 0,568 0,131 1/6m 41 ı ı 1.6 € £ ı ı Oum. Eff., PV 0.45 0.50 0.56 0.00 0.09 0.13 0.22 0.32 0.37 0.43 0.52 0.21 0.27 0.41 Eff., ml 248 816 140 340 442 607 672 669 737 847 911 0 62 207 357 520 Ş of Vol. o Eff., ml 0 38 52 85 65 41 78 64 62 78 67 92 87 27 31 Conc., mg/l 0.216 0.792 TCE 1 3.8 € ι S ŧ ١ ١ ١ 18 1 24 Cum. Eff., PV 0.09 0.22 0.29 0.30 0.40 0.43 0.54 0.00 0.03 0.25 0.47 0.07 0.51 Eff., ml 493 649 99/ 826 885 0 118 155 224 289 366 470 558 **697** 56 404 S. Vol. of Eff., ml 0 56 62 37 69 65 11 38 99 23 65 48 69 9 29 16 Conc., 0.842 0.189 89 mg/122 13E 1.2 1 $\frac{2}{2}$ t ı 1 Cum. Eff., PV 0.29 0.38 0.00 0.05 90.0 0.17 0.22 0.26 0,32 0.40 0.47 0.49 0.54 0.11 0.41 Eff., ml 0 75 901 180 270 293 354 468 522 657 699 762 797 877 431 611 C.E. Vol. of Eff., 0 46 8 75 3 53 11 37 54 89 83 35 31 19 601. 16 Ω 9 10 15 m 4 æ 3 14 Zay Tay 1

Table 89. Daily Data for Columns R7, R8, and R9.

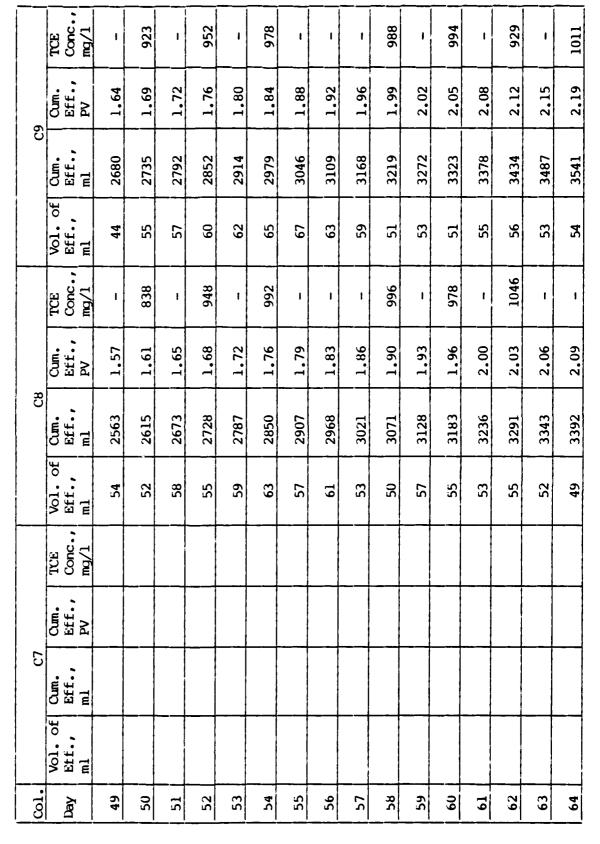
1 1		<i>C</i> 3				80	<u> </u>			60		
Vol.	· of	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/1	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc.,	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc.,
	99	943	0.58		40	925	0.57	ı	24	935	0.57	1
	78	1021	0.63	,	37	962	0.59	1	63	866	0,61	-
	50	1071	99.0	153	62	1024	0.63	33	50	1048	0.64	18
}	14	1085	0.67	1	38	1062	0.65	١	36	1084	99.0	•
}	89	1153	0.71	234	11	1133	0.70	78	50	1134	0.70	48
ł	37	1190	0.73		43	1176	0.72	1	41	1175	0.72	ı
1	71	1261	0.77	217	57	1233	0.76	113	71	1246	0.76	77
}	36	1297	0.80	,	31	1264	0.78	1	65	1311	0.80	1
į	70	1367	0.84	342	54	1318	0.81	154	09	1371	0.84	229
	29	1396	98.0	1	40	1358	0.83	t	57	1428	0.88	ı
	64	1460	0.90	325	50	1408	0.86	191	59	1487	0.91	406
1	19	1479	0.91	'	36	1444	0.89	l	53	1540	0.94	•
ļ	82	1537	0.94	396	11	1515	0.93	282	67	1607	0.99	497
İ	16	1553	0.95	ı	30	1545	0.95	1	29	1636	1.00	1
1	50	1603	96.0	408	63	1608	0.99	335	70	1706	1,05	615
ł	31	1634	1,00	1	37	1645	1.01	_	26	1732	1.06	

Table B9. Continued.

Table B9. Continued.

(•)

Vol. of Cum. Cum. TCE Vol. of Cum. Cum. Eff., Eff., Eff., Conc., Eff., E	Col.		C7				83				65		
57 1691 1.04 462 71 1716 1.05 39 1730 1.07 - 35 1751 1.07 50 1780 1.09 522 63 1814 1.11 56 1836 1.13 - 69 1883 1.16 63 1899 1.16 - 53 1936 1.19 59 1958 1.20 761 50 1986 1.22 54 2057 1.26 892 37 2065 1.27 56 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 Saturated 68 2308 1.45 (Removed from service) 59 2367 1.48 7 42 2462 1.51	≥		Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l		Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
39 1730 1.07 - 35 1751 1.07 50 1780 1.09 522 63 1814 1.11 56 1836 1.13 - 69 1883 1.16 63 1899 1.16 - 53 1936 1.19 59 1958 1.20 761 50 1986 1.24 46 2057 1.26 892 37 2065 1.27 56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 saturated 68 2367 1.45 (Removed from service) 59 2367 1.48 53 2420 1.48 64 2462 1.51	2	57	1691	1.04	462	71	1716	1.05	527	57	1789	1,10	653
50 1780 1.09 522 63 1814 1.11 56 1836 1.13 - 69 1883 1.16 63 1899 1.16 - 53 1936 1.19 59 1958 1.20 761 50 1966 1.22 46 2057 1.26 892 37 2065 1.24 56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 Saturated 68 2308 1.42 (kemoved from service) 59 2367 1.45 62 53 2420 1.48	34	39	1730	1.07	J	35	1751	1.07	1	42	1831	1.12	1
56 1836 1,13 - 69 1883 1,16 63 1899 1,16 - 53 1936 1,19 59 1958 1,20 761 50 1986 1,22 53 2011 1,23 - 42 2028 1,24 46 2057 1,26 892 37 2065 1,27 56 2113 1,30 - 54 2119 1,30 62 2175 1,33 886 58 2177 1,34 51 2226 1,37 - 63 2240 1,42 45 2271 1,39 saturated 68 2308 1,42 (Removed from service) 59 2367 1,48 53 2420 1,48	35	25	1780	1.09	522	63	1814	1.11	506	70	1901	1.17	682
63 1899 1.16 - 53 1936 1.19 59 1958 1.20 761 50 1986 1.22 53 2011 1.23 - 42 2028 1.24 46 2057 1.26 892 37 2065 1.27 56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.45 45 2271 1.39 Saturated 68 2308 1.45 (Nemoved from service) 59 2367 1.48 53 2420 1.48	- 6	56	1836	1.13	1	69	1883	1.16		99	1967	1.21	'
59 1958 1,20 761 50 1986 1,22 53 2011 1,23 - 42 2028 1,24 46 2057 1,26 892 37 2065 1,27 56 2113 1,30 - 54 2119 1,30 62 2175 1,33 886 58 2177 1,34 51 2226 1,37 - 63 2240 1,37 45 2271 1,39 Saturated 68 2308 1,42 (Removed from service) 59 2367 1,48 53 2420 1,48 53 2420 1,48 64 2462 1,51	37	63	1899	1.16	'	53	1936	1.19	1	53	2020	1.24	1
53 2011 1.23 - 42 2028 1.24 46 2057 1.26 892 37 2065 1.27 56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 Saturated 68 2367 1.45 (Kemoved from service) 59 2367 1.45 53 2420 1.48 53 2420 1.51 64 2462 1.51	8	59	1958	1.20	761	50	1986	1.22	541	57	2077	1.27	788
46 2057 1.26 892 37 2065 1.27 56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 *aturated 68 2308 1.42 (Kemoved from service) 59 2367 1.45 53 2420 1.48 53 2462 1.51	68	53	2011	1.23	1	42	2028	1.24	•	61	2138	1.31	1
56 2113 1.30 - 54 2119 1.30 62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 \$aturated 68 2308 1.42 (Removed from service) 59 2367 1.48 53 2420 1.48 64 2462 1.51	2	46	2057	1.26	892	37	2065	1.27	623	55	2193	1.34	812
62 2175 1.33 886 58 2177 1.34 51 2226 1.37 - 63 2240 1.37 45 2271 1.39 Saturated 68 2308 1.42 (Kemoved from service) 59 2367 1.45 53 2420 1.48 64 42 2462 1.51	1	56	2113	1.30	ı	54	2119	1.30	ı	59	2252	1,38	ı
51 2226 1.37 * - 63 2240 1.37 45 2271 1.39 Saturated 68 2308 1.42 (Removed from service) 59 2367 1.45 53 2420 1.48	2	62	2175	1,33	988	58	2177	1.34	744	55	2307	1.42	913
45 2271 1.39 * saturated 68 2308 1.42 (Removed from service) 59 2367 1.45 53 2420 1.48 42 2462 1.51	53	51	2226	1.37	Ì	63	2240	1.37	ı	53	2360	1.45	-
(Kernoved from service) 59 2367 1.45 53 2420 1.48 42 2462 1.51	44	45	2271	1,39	* Saturate	-	2308	1.42	852	46	2406	1.47	928
53 2420 1.48	45	(Kemov	from			59	2367	1.45	'	54	2460	1.51	1
42 2462 1.51	9					53	2420	1.48	803	58	2518	1.54	941
	-2					42	2462	1.51	•	99	2584	1.58	1
4/ 2509 1.54	48					47	2509	1.54	ı	52	2636	1.62	973



Continued. Table B9.

Table B9. Continued.

			 i	 -	 -			 -	<u></u>	-	— <u></u>						
	TCE Conc., mg/l	ı	ı	1	965	1	1022	1	1058	1	979	1	1092	ı	ı	-	1053
	Cum. Eff., PV	2.22	2.25	2.28	2,31	2.34	2.37	2.41	2.44	2.47	2.49	2.52	2,55	2,58	2.62	2,65	2.68
ව	Cum. Eff., ml	3593	3642	3689	3738	3788	3844	3897	3946	3994	4040	4090	4139	4186	4240	4293	4345
	Vol. of Eff., ml	52	49	47	49	20	56	53	49	48	46	20	49	47	54	53	52
	TCE Conc., mg/1	1	284	ı	•	1	1053	ı	941	,	966	ı	I	•	1018	,	985
	Cum. Eff., PV	2.12	2.16	2.19	2.22	2.26	2.29	2.32	2.36	2,39	2.42	2.45	2.47	2,50	2.54	2.57	2.60
83	Cum. Eff., ml	3443	3494	3548	3604	3655	3709	3762	3818	3867	3913	3961	4008	4057	4111	4162	4212
	Vol. of Eff., ml	50	52	54	56	51	54	53	56	49	46	48	47	49	54	51	20
	TVE Conc., mg/l																
	Cum. Eff., PV																
7.2	Cum. Eff., ml																
	Vol. ot Eft., ml																
©1.	Day	65	99	29	89	69	22	71	72	73	74	75	76	77	78	27	80

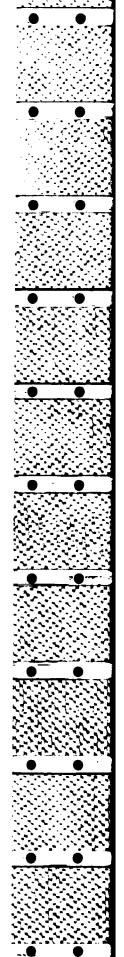


Table B9. Continued.

	TCE Conc., mg/1	1	1060	1	١	1	1056	١	1063	1	954	1	1040	1	1	1	1043
	Cum. Eff., PV	2.72	2.74	2.78	2.84	2.84	2.87	2.90	2.93	2.96	3.00	3.03	3.06	3.09	3,12	3.15	3,18
ව	Cum. Eff., ml	4399	4446	4497	4596	4596	4643	4694	4748	4801	4853	4906	4956	5007	5056	5103	5151
	Vol. of Eff., ml	54	47	51	51	48	47	51	54	53	52	53	20	51	49	47	48
	TCE Conc., mg/l	١	1025	1	1039	1	978	1	1019	1	1038	1	1021	'	1027	1	981
	Cum. Eff., PV	2.63	2.66	2,69	2.72	2.75	2.78	2.81	2.84	2.87	2,90	2,93	2.96	2.99	3.03	3.06	3.09
න	Cum. Eff., ml	4263	4311	4358	4413	4461	4508	4554	4599	4646	4694	4745	4798	4850	4904	4959	5010
	Vol. of Eff., ml	51	48	47	55	48	47	46	45	47	48	51	53	52	54	55	51
	TCE Conc., mg/l										-						
	Cum. Eff., PV																
7.3	Cum. Eff., ml														·		
	Vol. of Etf., ml																
501.	ray.	81	82	83	84	85	98	87	88	68	96	16	92	- 69	94	95	8

Conc., mg/1ı ı ı ı Cum. Eff., PV 3.68 3,43 3.46 3.49 3.55 3.62 3,65 3.34 3.40 3.52 3.59 3.24 3.27 3,31 3,37 3.21 of Eff., ml Vol. TCE Conc., mg/1ı ı ı ı • Cum. Eff., PV 3,59 3.19 3.22 3.25 3.28 3,34 3,38 3.40 3,43 3.47 3.50 3,53 3.56 3.31 ဆ Eff., ml SEM. Vol. of Eff., ml TCE Conc., mg/l Cum. Eff., PV $C_{\mathcal{I}}$ Eff., ml S. Vol. of Eff., ml Sol. y) Jay

Table B9. Continued.

Table B9. Continued.

<u> </u>		C7				83 C8				60		
Кеп	Vol. of Eff., ml	Oum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/1	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l
113					50	5866	3.62	1	50	9009	3.71	1
114					50	5916	3.65	1004	53	6029	3.74	1043
115					50	5966	3.68	t	51	6110	3.77	1
116					47	6013	3.71	1032	50	6160	3.80	1071
117					48	6061	3.74	ı	48	6208	3.83	1
118					48	6109	3.77	1	49	6257	3.86	ı
119					51	9190	3.80	l	52	6309	3.89	ı
120					50	6210	3,83	994	49	6358	3.92	1052
121					52	6262	3.87	1	47	6405	3,95	ı
122					51	6313	3.90	1017	53	6458	3.99	1017
123					50	6363	3.93	1	52	6510	4.02	ı
124					48	6411	3.96	1	49	6559	4.05	1
125					51	6462	3.99	1	50	6099	4.08	ı
126					47	6209	4.02	952	51	0999	4.11	1050
127					50	6559	4.05	l	48	6708	4.14	1
128					51	6610	4.08	1023	52	0929	4.17	1078

	O.M. TOE		SE SE	+	4.23	4.26	4.29 1016						<u></u>						
	63	or cuit.		53 6813	47 6860	46 6906	49 6955				+		1		+				
Table B9. Continued.		of Oum. TCE	Eff., Eff., Conc., ml PV mg/l	-	6029	0367	+-	50 6810 4.20											
		1100	Vol. of Cum. Eff., Conc.,	m] m] FV im/1	129	130	131		132										

Conc., 7.6 339 mg/1101 83 471 ı 1 £ £ ı ı ı Eff., PV 1.00 0.36 0.49 0.65 0.88 0.93 Cum. 0.00 0.04 0.23 0.57 0.81 **R12** Eff., 1635 1316 0 2 376 935 1180 1514 202 293 489 1061 1431 Cum. 581 of Vol. c Eff., ml 136 0 2 132 83 92 137 86 131 83 121 91 Conc., mg/l 0.190 ı ₽ 1 122 432 592 2.1 65 Cum. Eff., PV 0.95 0.00 0.46 0.73 0.79 0.05 0.30 0.38 0.60 99.0 0.90 0.12 0.25 0.52 0.84 R11 Eff., 919 1543 192 278 758 1083 1195 1283 1464 O.M. 0 75 408 851 1374 491 Vol. of Eff., ml 0 130 125 142 105 112 9 79 75 86 93 127 TCE Conc., mg/l 205 206 ı $\frac{1}{2}$ 웆 32 263 Cum. Eff., PV 0.00 0.05 0.10 0.16 0.24 0.43 0.64 98.0 0.91 0.30 0.51 0.57 **E**30 Eff., ml 165 400 695 833 1040 1162 1489 0 82 263 492 1400 ÇM. 241 1291 Vol. of Eff., ml 0 138 114 129 109 82 83 9/ 22 137 22 93 122 8 82 121 8 **9**[15 ~ S 9 ထ 9 10 13 14 Day 4 1

Table Bl0. Daily Data for Columns Rl0, Rl1, and Rl2.

C

Table Bl0. Continued.

(<u>•</u>

	TCE Conc., mg/l	ı	495	753	1	875	1	930	ı	1055	1	886	ı	1047	1	1024	-
2	Cum. Eff., PV	1.06	1.11	1.15	1.20	1.27	1.35	1.41	1.47	1.54	1.58	1.64	1.69	1.74	1.80	1.86	1,91
R12	Cum. Eff., ml	1727	1807	1881	1949	2077	2196	2299	2389	2506	2579	2668	2750	2833	2927	3032	3115
	Vol. of Eff., ml	92	80	74	89	128	119	103	06	117	73	89	82	83	94	105	83
	TCE Conc., mg/l	1	1	604	1	812	1	822	ı	818	•	942	1	982	1	915	•
	Cum. Eff., PV	1.01	1,08	1,14	1,19	1.24	1.31	1.38	1.44	1.49	1.53	1.60	1,66	1.74	1.80	1.87	1,93
R11	Oum. Eff., ml	1645	1767	1851	1939	2027	2130	2258	2347	2425	2499	2612	2706	2837	2927	3042	3141
	Vol. of Eff., ml	102	122	84	88	88	103	128	88	78	74	113	94	131	06	115	66
	TCE Conc., mg/l	1	390	646	1	069		802	ı	855	1	872	1	923	1	972	1
	Cum. Eff., PV	96*0	1.04	1.11	1.17	1,22	1.27	1,32	1,38	1,46	1.54	1.60	1.64	1.72	1.76	1.84	1.91
RIO	Cum. Eff., ml	1573	1696	1814	1906	1983	2064	2160	2247	2382	2508	2602	2681	2799	2874	3005	3119
	Vol. of Etf., ml	84	123	118	92	77	81	ક	87	135	126	25	79	118	75	131	114
Col.	Day	17	18	19	20	21	77	23	24	25	56	27	78	29	30	31	32

Table B10. Continued.

8	l I		l l			R11			1 1	R12	2	
Day	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/1	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc., mg/l	Vol. of Eff., ml	Cum. Eff., ml	Cum. Eff., PV	TCE Conc.,
33	123	3242	1.99	994	74	3215	1.97	1041	70	3185	1.95	1122
34	96	3338	2.05	ı	82	3297	2.02	1	122	3307	2.02	_
35	91	3429	2.10	1027	76	3373	2.07	1008	110	3417	2.09	1080
36	87	3516	2.16	1	71	3444	2.11	1	114	3531	2.17	-
37	95	3611	2.22	-	81	3525	2.16	ı	96	3627	2.22	-
38	109	3720	2.28	986	87	3612	2.22	1036	91	3718	2.28	1090
39	116	3836	2,35	1	94	3706	2.27	•	83	3801	2.33	ı
40	117	3953	2.42	1041	92	3798	2,33	1068	90	3891	2.39	1193
41	107	4060	2.49	ı	98	3896	2.39	1	81	3972	2.44	•
42	96	4156	2.55	1036	94	3990	2.45	ı	96	4068	2.50	1154
43	98	4242	2.60	1	109	4099	2.52	ŀ	92	4160	2.55	,
44	80	4322	2.65	1009	101	4200	2.58	993	103	4263	2,62	1120
45	88	4410	2.71	-	93	4293	2.63	ı	96	4359	2.69	ı
46	94	4504	2.76	1019	103	4396	2.70	1080	(Removed	from service	rice -	
47	108	4612	2.83	-	110	4506	2.76	•	broken.			
48	114	4726	2.90	979	137	4643	2.85	1026				

Continued.
B10.
Table

	TCE Conc., mg/l																
	Oum. Eff., PV																ţ.
R12	Cum. Eff., ml			_	-												
	Vol. of Eff., ml				-			-						·			
	TCE Conc., mg/l	1	1047	ı	1006	١	978	ı	1066	1	1079	1	1	1	975	-	1031
	Cum. Eff., PV	2.92	3.01	3.08	3.14	3.21	3.27	3,33	3,39	3.44	3.50	3,56	3.62	3.69	3.74	3.80	3.87
R11	Qum. Eff., ml	4767	4882	4990	5094	5195	5300	5396	5484	5578	5676	5772	5868	5970	6065	6159	6264
	Vol. of Eff., ml	124	115	108	104	101	105	96	88	94	86	96	96	102	95	94	105
	TCE Conc., mg/l	1	1020	1	,	-	1054	•	1043	ı	1012	1	1038	!	ı	1	1136
	Cum. Eff., PV	2.97	3.06	3.13	3.20	3.26	3.32	3.37	3.43	3.49	3.55	3.61	3.67	3.73	3.80	3.87	3.94
RIO	Cum. Eff., ml	4847	4960	5072	5178	5278	5373	5466	5554	5648	5744	5843	5946	6050	6159	6270	6377
	Vol. of Eff., ml	121	113	112	106	100	95	93	88	94	96	66	103	104	109	111	107
\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	Day	49	- 20	-21	52	53	54	55	26	57	58	59	09	- 19	62	63	64



	R10 Cum.		TCE	Vol. of	R11		TCE	Vol. of	ſ	R12 Oum.	TCE
E E	Eff., ml	Eff., PV	Conc., mg/l	Eff., ml	Eff., ml	Eff., PV	Conc., mg/1	Eff., ml	Eff., ml	Eff., PV	Conc., mg/l
1	6482	4.00	1	103	6367	3.93	ı				
	6581	4.06	1032	104	6471	3.99	1				
	6681	4.12	-	86	6569	4.05	1				
	6787	4.19	-	96	6665	4.11	1012				
	6895	4.26	-	86	6763	4.17	•				
	9669	4.32	866	92	6855	4.23	296				
	7105	4.39	I	95	6950	4.29	ı				
	7210	4.45	1046	66	7049	4.35	1018				
	7311	4.51	ı	105	7154	4.42	l				
	7406	4.57	1023	86	7252	4.48	992				
-	7506	4.63	1	96	7348	4.54	ı				
	7603	4.69	1038	103	7451	4.60	1078				
	7699	4.75	ı	100	7551	4.66	t				
	7790	4.81	1011	104	7655	4.73	963				
-	7886	4.87	-	101	7756	4.79	ı				
	7992	4.93	982	97	7853	4.85	1014				





Table Bl0. Continued.

Bay Vol. of Cum. Eff., Eff., Conc. ml Cum. Eff., Eff., Conc. ml 81 101 8093 5.00 - 82 97 8190 5.06 103 84 105 8393 5.12 - 85 103 8496 5.24 - 86 99 8595 5.31 100 8797 5.33 100 89 8697 5.37 - 89 96 8893 5.49 - 90 95 8988 5.55 97 91 93 9081 5.61 - 92 103 9184 5.67 102 93 104 9288 5.73 - 94 106 9394 5.86 - 95 8988 5.73 - 91 93 9081 5.61 - 94 106 9394 5.86 - 9		R11				R12	Ì
101 8093 5.00 97 8190 5.06 1 105 8393 5.12 1 105 8393 5.18 1 103 8496 5.24 1 99 8595 5.31 1 100 8797 5.43 1 96 8893 5.49 5.49 95 8988 5.55 5.61 103 9184 5.61 1 104 9288 5.73 1 106 9394 5.86 1 101 9495 5.86 5.86	TCE Vol. Conc., Eff., mg/l ml	of Cum. Eff., ml	Oum. Eff., PV	TCE Conc., mg/l	Vol. of Cur Eff., Ef ml ml	Cum. Cum. Eff., Eff., ml PV	rce Conc., mg/l
97 8190 5.06 1 98 8288 5.12 1 105 8393 5.18 1 103 8496 5.24 1 104 8595 5.31 1 100 8797 5.49 5.49 96 8893 5.49 5.49 95 8988 5.55 93 9081 5.61 104 9288 5.73 106 9394 5.80 101 9495 5.86	96 - 0	7949	4.91	-			
98 8288 5.12 105 8393 5.18 1 103 8496 5.24 1 102 8697 5.37 1 100 8797 5.43 1 96 8893 5.49 1 95 8988 5.55 1 93 9081 5.61 1 103 9184 5.67 1 104 9288 5.73 1 106 9394 5.86 1 101 9495 5.86 5.86	1037 99	8048	4.97	1063			
105 8393 5.18 1 103 8496 5.24 99 8595 5.31 1 102 8697 5.37 1 96 8893 5.49 5.43 95 8988 5.55 93 9081 5.61 103 9184 5.67 1 104 9288 5.73 106 9394 5.86	- 102	8150	5.03	'			
103 8496 5.24 99 8595 5.31 1 102 8697 5.37 1 100 8797 5.43 5.49 96 8893 5.49 5.49 95 8988 5.55 5.61 103 9184 5.61 1 104 9288 5.73 1 106 9394 5.86 5.86	1003 103	8253	5.09	1153			
99 8595 5.31 1 102 8697 5.37 100 8797 5.43 96 8893 5.49 95 8988 5.55 93 9081 5.61 103 9184 5.67 1 104 9288 5.73 106 9394 5.86 101 9495 5.86	- 109	8362	5.16	1			
102 8697 5.37 100 8797 5.43 96 8893 5.49 95 8988 5.55 93 9081 5.61 103 9184 5.61 104 9288 5.73 106 9394 5.86 101 9495 5.86	1019 103	8465	5,23	1047			
100 8797 5.43 96 8893 5.49 95 8988 5.55 93 9081 5.61 103 9184 5.67 1 104 9288 5.73 106 9394 5.86 101 9495 5.86	, – 106	8571	5,29	ı			
96 8893 5.49 95 8988 5.55 93 9081 5.61 103 9184 5.67 1 104 9288 5.73 106 9394 5.86 101 9495 5.86	984 97	8998	5,35	1059			
95 8988 5.55 93 9081 5.61 103 9184 5.67 1 104 9288 5.73 106 9394 5.86 101 9495 5.86	66 –	8767	5.41	1			
93 9081 5.61 103 9184 5.67 104 9288 5.73 106 9394 5.80 101 9495 5.86	96 626 6	8865	5.47	1033			
103 9184 5.67 104 9288 5.73 106 9394 5.80 101 9495 5.86	96 -	8961	5,53	1			
104 9288 5.73 106 9394 5.80 101 9495 5.86	1026 99	0906	5.59	1018			
106 9394 5.80 101 9495 5.86	- 102	9162	5.66	ı			
101 9495 5.86	968 104	9566	5.72	1043			
	- 105	9371	5.78	'			
96 98 9593 5.92 95	952 101	9472	5.85	1019			

| Col. | Rio | Com. | Rio | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Cont. | Co

Conc., Cum. Eff., **R12** Cum. Eff., ml Vol. of Eff., ml TCE Conc., mg/1 Oum. Eff., PV 6.89 6.95 7.26 7,38 7,13 7,32 7.44 7.50 7.63 7.69 7.75 7.01 7.07 7.20 7.57 7.81 R11 Vol. of Eff., Conc., mg/1ŧ ı ŧ ł Cum. Eff., PV 7.40 7.89 7.03 7.09 7.46 7.65 6.97 7.28 7.52 7.59 7.22 7.34 7.71 7.77 7.83 Cum. Vol. of Etf., m Day

Table Bl0. Continued.

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	TCE Conc., mg/1						,		i I			
R12	Cum. Eff., PV											
2	Cum. Eff., ml											
	Vol. of Eff., ml											
	TCE Conc., mg/1	ı	351	ı	293							
	Cum. Eff., PV	7.87	7.93	7.99	8.05		-					
R11	Cum. Eff., ml	12751	12846	12942	13045							
:	Vol. of Eff., ml	97	95	96	103							
	TCE Conc., mg/l		417	1	403							
	Cum. Eff., PV	7.96	8.02	80.8	8,14							
R10	Oum. Eff., ml	12893	12995	13090	13184	-						
	Vol. of Eff., ml	104	102	95	94							, ,
CO1.	Day	129	130	131	132							

Table Bl0. Continued.



Q.

Table Bll. Daily Effluent Volume from Russell Soil Control Column.

			r	·•	
D	Effluent	D	Effluent	Don	Effluent Colleged ml
Day	Collected, m	l Day	Collected, ml	Day	Collected, ml
1	0	24	121	47	108
2	32	25	*120	48	106
3	*77	26	103	49	110
4	130	27	91	50	105
5	68	28	90	51	101
6	117	29	84	52	103
7	135	30	71	53	95
8	106	31	95	54	96
9	85	32	86	55	93
10	98	33	98	56	91
11	125	34	93	57	*88
12	*123	35	*94	58	86
13	103	36	89	59	80
14	111	37	99	60	94
15	137	38	92	61	97
16	115	39	87	62	95
17	122	40	96	63	102
18	129	41	108	64	106
19	*116	42	118	65	109
20	144	43	131	66	111
21	136	44	120	67	112
22	127	45	113	68	109
23 *Ind	139 icates sample	46 taken 1	104 for TCE analys	69 is. No	106 TCE detected

*Indicates sample taken for TCE analysis. No TCE detected in any samples.

Table Bll. Continued.

1	Effluent	<u> </u>	Effluent		Effluent
Day	Collected, ml	Day	Collected, ml	Day	Collected, ml
70	107	93	99	116	98
71	103	94	97	117	100
72	105	95	95	118	*101
73	97	96	94	119	103
74	96	97	96	120	102
75	100	98	99	121	107
76	102	99	104	122	101
77	94	100	97	123	98
78	97	101	98	124	96
79	103	102	98	125	*97
80	98	103	102	126	99
81	100	104	101	127	102
82	97	105	99	128	100
83	104	106	*101	129	*104
84	*101	107	102	130	98
85	96	108	96	131	102
86	95	109	98	132	103
87	94	110	99		
88	94	111	101		
89	98	112	100		
90	106	113	102		
91	102	114	98		
92 *Ind	103	115	96 for TCE analysi	s No	TCE detected

^{*}Indicates sample taken for TCE analysis. No TCE detected in any samples.

Table Bl2. TCE Time of Saturation

Time of Contact, hours	TCE Concentration (as fraction of maximum TCE solubility in water, 1100 mg/l)
0.5	0.183
1.0	0.196
1.5	0.164
2.0	0.207
3.0	0.268
4.0	0.294
5.0	0.463
7.5	0.588
10.0	0.601
13.0	0.660
17.0	0.705
24.0	0.896
28.0	1.024
36.0	0.983
48.0	0.972
53.0	0.990

	<u>ن</u>		Control	6.45	6.27	6.78	7.33	6.84	7.22	6.07	6.50	5.99	6.47	6.62	7,31	06.90	5.92	6.34	99.9	6.71	
			C12	5.97	6.21	68.9	6.28	6.35	6.36	7.28	6.12	6.27	7.31	6.38	6.47	6.29	5.76	6.42	6.47	7.59	
		ent.	c11	6.28	7.21	7.23	6.17	6.82	7.16	5.93	6.81	5.80	6.19	6.40	6.34	6.82	7.39	6.68	6.46	6.37	
		Effluent	C10	6.38	6.79	7.11	5.92	6.12	5.90	I	ı	l	ı	ı	ı	1	I	1	ı	1	
		Column	63	6.31	6.12	6.78	7.23	6.18	6.82	69.9	7.25	7.30	7.15	6.39	6.43	6.71	6.23	6.59	6.32	7.27	
		Soil (82	6.15	6.23	90.9	6.47	6.62	6.41	7.21	6.48	6.35	6.25	6.64	6.93	7.12	69.9	5.85	91.9	6.19	,
O.		Chalmers	22	7.25	6.67	6.28	6.83	6.46	6.74	6.33	6.19	7.27	68.9	7.35	7.49	6.65	6.17	6.58	98.9	ı	
		of Ch	90	6.61	6.28	6.12	6.57	6.15	6.19	5.82	5.93	6.87	6.26	6.47	6.81	7.08	6.67	6.31	6.24	6.28	
		3. pH	C5	6.02	6.24	5.83	6.22	6.20	6.31	7.19	6.34	6.65	6,81	6.03	5.62	6.54	7.27	6.74	5.99	08.9	1
		Table Bl	C4	56 6.26	91 6.19	43 6.09	4 6.03	85.9 61	17 5.97	21 6.13	37 6.21	22 5.86	33 6.28	63 6.34	4 6.61	58 6.72	70 6.37	46 6.21	15 5.83	9 6.22	•
		.	c2 c3	6.23 6.5	6.39 5.9	.72 6.	5.12 6.1	.33 5.8	.62 6.	.93 6.	.38 6.	.24 6.	.35 6.	.41 6.	5.32 6.7	.73 6.	.61 5.	.39 6.	.26 6.3	.38 6.2	1
			C1	9 60.9	6.17	6.13 6	6.39 6	9 50.9	6.16 6	6.42 5	6.23 5	6.30 6	6.59	5.94 6	6.36 5	6.63 5	6.91 6	6.27 6	5.52 6	6.33 6	
•			рах	4	14	21	29	36	44	53	62	70	97	82	8 8	94	100	106	114	122	

Table B14. pH of Russell Soil Column Effluent.

Dаχ	EZ	R2	R3	R4	RS	R6	R7	88	83	R10	R11	R12	Control
m	6.36	6.20	6.14	6.63	6.27	6.73	80.9	5.92	6.19	6.32	6.25	5.95	6.42
13	6.12	6.28	6.39	6.51	6.16	6.27	6.17	6.14	6.23	6.20	5.97	6.40	90.9
24	6.29	6.35	6.42	6.17	6.12	6.19	6.14	6.28	6.81	6.48	6.14	6.36	00.9
32	5.95	6.41	6.46	6.24	6.22	6.48	6.21	6.15	6.10	6.19	6.01	6.82	5.87
39	6.27	6.11	6.39	6.32	6.45	65.9	6.30	6.03	6.02	6.17	5.90	6.01	6.48
47	6.49	5.91	5.74	6.41	6.29	6.17	ı	60.9	5.97	6.25	80.9	t	6.67
54	7.23	6.58	6.12	6.64	7.23	6.35	t	6.04	6.85	6.16	6.22	ı	6.15
63	6.42	6.41	6.26	6.20	6.40	6.16	ı	6.15	6.27	6.08	5.94	ı	6.72
71	6.28	6.32	6.19	5.81	6.63	6.46	ı	6.21	6.44	6.25	6.23	ı	6.43
77	6.34	80.9	6.36	6.17	6.38	6.55	ı	5.83	6.63	90.9	6.44	ı	5.91
83	5.62	6.81	6.28	6.43	6.19	6.23	1	6.34	6.49	6.34	6.29	1	6.57
06	6.18	6.23	7.37	6.29	5.92	6.51	1	6.26	98.9	5.90	6.82	1	6.63
98	6.82	5.41	6.46	7.16	5.71	6.34	1	6.38	6.67	5.84	6.64	ı	6.52
101	6.91	5.62	6.54	6.58	6.83	6.03	ı	6.27	06.9	5.91	6.85	1	6.03
107	6.47	5.79	6.30	6.91	6.40	6.32	1	6.75	7.25	6.15	99.9	1	6.14
115	6.65	6.68	6.25	6.80	6.57	6.65	ı	6.89	6.45	6.31	7.21	1	6.44
123	6.58	6.52	6.50	6.40	6.29	6.83	1	7.16	6.51	6.20	6.32	1	5.98
1 29	6.11	6.34	60.9	6.33	5,96	6.40	ı	7.5	9	6 67	6.27	ı	30.0

Table B15. Effluent Volume and TCE Concentrations Used to Determine TCE Eluted from Columns by Simpson's Approximation.

	TC	E Con	centrat	ion, mg,	/l (fro	m Fig	ures 15	-22)
Cum. Eff. Vol., l	C1-3	C4-6	C7-9	C10-12	R1-3	R4-6	R7-9	R10-12
0.00	0	0	0	0	0	0	0	0
0.33	0	0	0	0	0	0	0	0
0.67	0	0	5	2	2	2	5	15
1.00	3	10	22	25	22	15	35	60
1.33	50	32	80	150	80	70	205	250
1.67	155	100	270	300	275	200	465	480
2.00	235	210	435	450	432	350	710	715
2.33	325	312	530	570	560	440	865	860
2.67	405	420	690	670	670	620	940	945
3.00	500	510	780	760	760	760	970	1000
3.33	600	615	845 905	835 900	840	850 915	990	1015
3.67 4.00	680 790	730 810	950	950	910 960	950	1005 1005	1040 1040
4.33	820	850	985	990	1010	925	1010	1035
4.67	830	880	1020	1005	1035	980	1015	1035
5.00	780	860	1035	1010	1045	980	1030	1035
5.33	700	815	1050	1010	1035	960	1030	1035
5.67	660	720	1050	1000	960	940	1035	1032
6.00	590	670	1050	990	840	910	1040	1030
6.33	503	605	1050	985	755	860	1040	1030
6.67	470	550	1050	980	670	800	1040	1030
7.00		510		980		720		1030
7.33		470		990		635		1030
7.67		430		990		520		1030
8.00		400		995		440		1030
8.33		370		1000		370		1030
8.67		340		990		315		1030
9.00		320		975		265		1028
9.33		295		950		230		1028
9.67		270		915		195		1028
10.00		240		875		170		1020
10.33		215 205		830 770		150 130		990
10.67		180						940
11.00 11.33		160		715 640		110 105		870 800
11.33		140		570		80		710
12.00		120		510		65		610
12.33		105		450		55		530
12.67		100		400		40		460
13.00		98		340		35		395

Table B16. Cumulative Mass of TCE Eluted from Chalmers Soil Columns.

Cum.	TCE Eluted in Column Group							
	C1-3	C1-3		C4-6		C7-9		C10-12
Eff. Vol., l	Mass, g	8	Mass, g	8	Mass, g	8	Mass, g	8
0.00 0.33 0.67 1.00 1.33 1.67 2.00 2.33 2.67 3.00 3.33 3.67 4.00 4.33 4.67 5.00 5.33 5.67 6.00 6.33 7.67 8.00 8.33 8.67 9.00 9.33 9.67 10.00 10.33 10.67 11.00 11.33 11.67 12.00 11.33 11.67 12.00 11.33 11.67 12.00 11.33 11.67 12.00 11.33 11.67 12.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00 11.33 11.67 11.00	0.20 0.32 0.46	0.0 0.0 0.0 0.1 0.5 1.5 2.7 4.4 6.3 8.9 11.8 22.5 26.2 29.5 32.6 35.3 37.9 40.3	0.16 0.28 0.44	0.0 0.0 0.1 0.1 1.1 2.3 6.5 1.6 1.5 1.9 2.7 2.6 2.7 3.0 3.1 4.1 4.1 4.1 4.1 4.1 4.1 4.1 4	0.35 0.55 0.80	0.0 0.0 0.1 0.1 0.5 1.4 2.4 3.8 5.5 7.3 9.3 11.4 13.6 15.8 18.2 20.5 22.9 25.3 27.7 30.0	0.01 0.03 0.10 0.23 0.40 0.60 0.84 1.10 1.39 1.69 2.02 2.34 2.68 3.01 3.34 3.67	0.0 0.0 0.0 0.1 0.2 0.6 7.5 1.6 1.8 1.6 1.8 1.6 1.8 1.6 1.8 1.6 1.8 1.8 1.8 1.8 1.8 1.8 1.8 1.8

Table B17. Cumulative Mass of TCE Eluted from Russell Soil Columns.

Cum. Eff. Vol., 1	TCE Eluted in Column Group								
	R1-3		R4-6		R7-9		R10-12		
	Mass, g	8	Mass, g	8	Mass, g	8	Mass, g	8	
0.00 0.33 0.67 1.00 1.33 1.67 2.00 2.33 2.67 3.00 3.33 3.67 4.00 4.33 4.67 5.00 5.33 5.67 6.00 6.33 6.67 7.00 7.33 7.67 8.00 8.33 8.67 9.00 9.33 9.67 10.00 11.33 11.67 12.00 11.33 11.67 12.00 12.33 12.67 13.00	0.00 0.00 0.01 0.02 0.07 0.20 0.35 0.56 0.79 1.06 1.35 1.66 1.98 2.33 2.66 3.01 3.34 3.64 3.90 4:04	0.0 0.0 0.0 0.1 0.3 1.0 2.7 4.8 7.7 10.8 14.5 18.5 22.7 27.1 31.9 36.4 41.2 45.8 49.9 53.4 55.3		0.0 0.0 0.0 0.1 0.1 13.2 13.0 17.1 225.7 13.0 17.1 225.7 13.0 17.1 12.1 13.0 13.0 13.0 13.0 13.0 13.0 13.0 13	0.00 0.01 0.01 0.04 0.15 0.34 0.61 0.91 1.22 1.55 1.88 2.21 2.54 2.87 3.21 3.55 3.89 4.24 4.58 4.92	0.0 0.1 0.3 1.0 2.3 4.2 6.2 8.4 10.6 12.9 17.4 19.7 22.0 24.3 26.6 29.0 31.4 33.7	0.00 0.02 0.03 0.06 0.18 0.37 0.64 0.94 1.26 1.59 1.27 2.62 2.96 3.36 4.37 5.38 6.36 6.71 7.04 7.72 8.40 8.74 9.35 9.88 10.44 10.47	0.0 0.1 0.0 1.2 1.2 4.4 6.6 13.5 17.9 22.6 4.3 15.9 22.6 24.9 27.6 29.6 48.6 29.6 48.6 29.6 48.6 48.6 59.7 48.6 48.6 59.7 59.6 69	

Table B18. Cumulative Mass of TCE Eluted Based Upon Comparison to a CSTR (53).

CEV,a	Chalmers % Eluted	Russell % Eluted	CEV,	Chalmers % Eluted	Russell % Eluted
0.00	0	0	3.9	90	91
0.05	3	3	4.2	91	93
0.1	6	6	4.5	93	94
0.2	11	12	4.8	94	94
0.3	16	17	5.1	95	96
0.4	21	22	5.4	96	96
0.5	25	27	5.7	96	97
0.6	29	31	6.0	97	98
0.7	33	35	6.3	97	98
0.8	37	39	6.6	98	98
0.9	41	43	6.9	98	99
1.2	50	52	7.2	98	99
1.5	58	60	7.5	99	99
1.8	65	67	7.8	99	99
2.4	75	77	8.4	99	99
2.7	79	81	8.7	99	100
3.0	83	84	9.0	99	-
3.3	85	87	9.3	100	-
3.6	88	89			

Note: aCEV = Cumulative Effluent Volume



Table B19. Ammonia Concentrations in Soil Column Effluents.

	Ammonia Concentration, mg/l, for indicated da								
Col.	Day 71	Day 78	Day 83	Day 87	Day 92	Day 97			
Chalm	ers So	il							
CC *C1 C2	0.39 0.72 0.63	0.31 0.51 0.68	0.44 0.87	0.37 1.41	0.29 2.86	0.48 3.97 0.83		0.28 9.73 0.56	0.36 7.62
C3 C4	0.88 0.75	0.52 0.61	_	- -	0.49 0.53	-	0.72	0.51 0.44	-
C5 C6 *C7	0.59 0.58 0.69		4.95 - 0.72	8.73 0.68 1.96	7.91 - 1.74	8.23 - 2.94		7.49 0.32 8.33	2.12 - 9.14
C8 C9 C10	0.60 0.46 Remov	0.55 0.52 ed fro	- - m serv	0.77 - ice on	- - Day 4	- 0.68	0.71	0.58 0.57	-
*C11 C12	0.61		2.84				10.6	5.53 0.49	3.16
Russe	ll Soi	<u>1</u>							
RC *R1 R2 R3 *R4 R5 R6 R7			0.39 - 0.83 - m serv	0.42 0.96 - 3.46 0.56 - ice on		2.14 0.35 - 5.93 - -	10.3 - 0.43 8.78 -	0.25 8.91 0.52 0.39 3.92 0.37 0.54	0.34 7.40 - 3.14
*R8 R9 *R10 R11 R12	0.39 0.27 0.31 0.42 Remov	0.52 0.46 0.55 0.62 ed fro	0.65 - 0.86 - m serv	1.83 0.35 2.57 0.73 ice on	1.74 7.13 Day 4	6.19	12.2 - 9.42 0.58	5.20 0.31 3.71 0.53	1.94

^{*}Indicates columns to which 10~mg/l ammonia nitrogen added to water applied to columns for Days 75-100.

Table B20. Nitrate Concentrations in Soil Column Effluents.

	Nitrat	e Concer	ntration,	mg/l,	for indicated	d days
Col	Day 64	Day 73	Day 78	Day 84		Day 105
Chalme	rs Soil					
сс	0.42	0.56	0.85	0.74	0.53	0.69
*C1	_	0.21	0 16	0.19	0.92	0.52
C2	-	0.23	0.27	-	0.39	0.57
C3	-	0.20	0.22	0.31	-	0.28
C4	_	0.27	0.21	_	_	0.30
*C5	_	0.21	0.19	0.23	0.80	0.96
C6	_	0.20	0.23	_	-	0.32
*C7	_	0.28	0.22	0.25	0.43	0.58
C8	_	0.19	0.32	_	0.49	0.34
C9	_	0.24	0.28	0.22	-	0.35
C10	Removed		cvice on	Day 44.		
*C11	-	0.22	0.27	0.34	0.72	0.79
C12	-	0.23	0.29	_	-	0.14
Russel	1 Soil					
RC	0.63	0.90	0.87	0.71	0.68	0.46
*R1	-	0.19	0.26	0.36	0.40	0.62
R2	-	0.22	0.25	_	0.16	0.18
R3	-	0.20	0.15	0.24	-	0.26
*R4	-	0.19	0.23	0.27	0.63	0.77
R5	-	0.26	0.31	-	0.39	0.33
R6	-	0.24	0.36	-	-	0.14
R7	Removed	from sea	cvice on	Day 44.		
*R8	-	0.21	0.37	0.18	0.52	0.77
R9	-	0.19	0.19	0.25	-	0.22
*R10	-	0.23	0.16	0.65	0.87	0.54
R11	-	0.20	0.25	-	-	0.36
R12	Removed	from ser	rvice on	Day 45.		

^{*}Indicates columns to which 10 mg/l ammonia nitrogen added to water applied to columns for Days 75-100.

Table B21. Chloride Concentrations in Soil Column Effluents.

	Chloride Concentrations, mg/l, for indicated da									
Col.	Day 66	Day 72	Day 79	Day 86	Day 94		Day 110	Day 119	Day 127	
Chalme	ers So	<u>i 1</u>								
СС	1.2	2.8	2.1	3.2	1.9	2.4	2.2	1.6	1.0	
*C1	1.9	4.1	9.6	7.1	5.9	6.8	4.2	4.9	3.2	
C2	3.9	3.7	5.2	6.1	4.8	5.1	6.3	5.4	5.8	
C3	2.4	2.9	4.6	3.7	4.2		3.8	5.1	4.0	
C4	3.1	2.2	1.8	3.3	3.9	4.1	3.3	4.2	4.8	
*C5	3.6	5.6	2.8	8.7	6.9	7.5	8.5	4.7	5.9	
C6	1.7	2.2	3.0	3.8	2.1	4.1	<1.0	3.6	4.2	
*C7	4.1	6.9	7.4	9.7	11.4	7.8	12.2	9.0	_	
C8	2.3	2.9		3.5	2.0	3.2	2.2	2.8	1.1	
C9	2.9	1.1	1.4	2.6	1.0	3.6	4.1	2.0	1.4	
C10	Remov	red fro	om ser	vice o	n Day	44.				
*C11	3.8	10.1	6.4	8.8	12.1	9.4	7.8	9.1	7.4	
C12	1.4	1.6	3.1	3.5	4.0	4.8	4.0	2.2	3.6	
Russe	l Soi	<u>L</u>								
RC	2.2	3.1	1.2	1.9	<1.0	1.5	1.5	1.1	1.4	
*R1	4.8	5.0	7.3			6.6	7.2	8.4	9.6	
R2	3.7	2.1		4.6	7.9 3.2	2.8	2.6	1.3	2.4	
R3	2.3	2.5	3.2	1.9	2.9	2.8	3.0	<1.0	1.4	
*R4	6.2	3.6	3.9	7.0	10.2	5.9	4.8	6.2	6.7	
R5	1.6	2.2	4.2	3.3	4.6	3.4	3.8	3.0	2.4	
R6	1.8 .	2.2	3.1	1.2	3.6	4.2	4.4	2.8	<1.0	
R7	Remov	ed fro	m ser	vice o						
*R8	2.8			7.6			9.4	8.6	6.9	
R9	2.4	3.6	4.4	5.3			1.8	3.5	2.8	
R10	1.4	3.9	6.9	5.1	4.0	8.4	7.4	8.5	8.1	
R11	2.7	1.8	2.0	4.2	1.2	3.2	2.4	1.4	3.6	
R12	2.7	1.8	2.0	4.2	1.2	3.2	2.4	1.4	3.6	
R12	Remov	ed fro	om ser	vice o	n Dav	45.				

^{*}Indicates columns to which 10 mg/l ammonia nitrogen added to water applied to columns for Days 75-100.

Appendix C. Tabulated Data from TCE:Soil Adsorption Studies.

Table Cl. Data For Determination of Soil Adsorption Isotherms.

Coa	arse Pa	rticle S	ize	Fine	Particl	e Size
C _i , mg/l	*Vl,	*M,	+X,	*V1,	*M, g	⁺ Х, и д
Chalme	ers Soi	<u>1</u>				
110 220 440 660 880 1100	20.4	10.143 10.192 10.098 10.078 10.192 10.018	426 744 1656 2963 3129 3997	20.5 20.6 21.0 20.3 20.4		1548 2350 4343 4950 7341
Russe	ll Soil					
110 220 440 660 880 1100	20.5	10.313 10.074 10.168 10.071	326 330 816 1271 1833 2530	20.4 20.5 20.7 20.1 20.6 20.4	9.979 10.094 10.130 10.146 10.080 10.118	469 616 1408 1806 2631 4472

^{*}Average of two values.

NOTE: Information from this table used in conjunction with $\rm C_{\rm e}$ and $\rm C_{\rm b}$ values of Table 23 to calculate X/M values of Table 23.

⁺Calculated from average values.

Table C2. Data For Determination of X/M Values In Time of Adsorption Experiment.

 Time,	<u>Ci=</u>	= 220 mg/	<u>/1</u>	Ci =	880 mg	<u>/1</u>
Hours	*V1,	*M,	+x,	*V1,	*M,	+x,
nours	ml	g	ųg ųg	ml	g	# g
 						
Chalmer	s Soil	., Coarse	Partic	le Size		
2	20.2	10.131	182	20.8	9.942	457
4	20.3	10.187	162	20.7	10.168	580
6	20.1	9.829	462	20.4	10.210	1654
9	20.0	10.009	620	20.6	10.164	2287
13	20.1	10.039	763	20.7	10.103	2960
23	20.2	10.215	808	20.4	10.134	3182
33	20.5	10.127	738	20.5	10.130	3424
48	21.0	10.111	819	20.7	9.967	3229
Chalmer	s Soil	., Fine	Particle	Size		
2	20.6	9.986	494	20.4	10.149	1591
4	20.5	10.093	963	20.5	10.088	3054
6	20.2	10.236	1010	20.6	9.894	3605
9.5	20.6	9.841	1256	20.4	10.136	4998
13	20.4	10.108	1265		10.034	5166
16	20.4		1326	20.3	10.217	5399
24			1374	20.6	10.118	5520
36	20.3	9.903	1299	20.4	10.302	5650
48	20.6	9.873	1195	20.4	10.104	5222
Russell	Soil,	Coarse	Particle	Size		
2	20.2	10.121	81	20.4	10.039	306
4	20.3	10.110	142	20.3	10.174	365
6	20.3	10.125	243	20.2	10.116	889
9	20.5	10.127	226		10.143	1258
14		10.139	365	20.5	9.972	1742
18		10.193	571	20.2	10.218	1899
24		10.146	487	20.4	10.193	1816
38	20.2	10.211	470	20.3	10.106	1860
48	20.5	10.012	512	20.1	10.088	1930

Table C2. Continued.

Time,	<u>Ci</u>	= 220 mg/	<u>/1</u>	<u>Ci</u>	= 880 mg	<u>/1</u>
Hours	*Vl, ml	*M,	⁺ Х, µ9	*Vl, ml	*M,	+x, yg
Russe	ll Soil	, Fine Pa	article	Size		
2	20.4	10.016	163	20.3	10.136	710
4	20.2	10.127	263	20.5	9.986	779
6	20.3	10,108	487	20.5	10.014	2193
	20.5	9,992	656	20.2	10.190	2362
10						2699
10 15	20.2	10.139	727	20.6	9.89/	2.07
	20.2	10.139 10.201	727 751	20.6	9.897 10.029	
15		10.201	751	20.4	10.029	289
15 24	20.3	•		-	10.029 10.201	289° 2984 271°

Average of two values.

NOTE: Information from this table used in conjunction with $C_{\rm e}$ and $C_{\rm b}$ values of Table 26 and 27 to calculate appropriate X/M values.

⁺ Calculated from average values.

Table C3. Data for Determination of Glass Adsorption Isotherm.

C _i , mg/l	Vl, ml	Mg, g	Χ, μg	Ag cm2
220	125.3	78.161	626	537
440	125.5	74.870	376	514
660	126.0	76.212	-1003	524
880	125.4	75.961	-1630	522
1100	124.2	76.323	124	528

Surface area of glass bead = $0.503 \text{ cm}^2/\text{bead} = \text{SA}$ Mass of one glass bead = 0.0732 g/bead = MGB

 $SA = 0.503 \text{ cm}^2/\text{bead} = 6.87 \text{ cm}^2/\text{g}$ MGB = 0.0732g/bead Ag = Area of glass beads

Mg = Mass of glass beads

 $Ag = Mg \times 6.87 \text{ cm}^2/g$

Area of glass exposed in column is that of a cylinder 8 cm in diameter and 35" (88.9 cm) long.

Area = πx D x L = πx 8 x 88.9 = 2234 cm²

Table C4. Data for Determination of Gravel Adsorption Isotherm.

Vl, ml	Mgr, g	Χ, μg	
136.5	71.24	137	
136.0	70.78	-816	
136.0	76.52	408	
134.2	76.00	-268	
134.4	78.40	941	
133.6	76.49	267	
133.8	78.63	535	
	ml 136.5 136.0 136.0 134.2 134.4 133.6	ml g 136.5 71.24 136.0 70.78 136.0 76.52 134.2 76.00 134.4 78.40 133.6 76.49	ml g μg 136.5 71.24 137 136.0 70.78 -816 136.0 76.52 408 134.2 76.00 -268 134.4 78.40 941 133.6 76.49 267

Mass of gravel in 2" length of $80\,\mathrm{mm}$ i.d. tubing is approximately $369\,\mathrm{g}$.

Appendix D. Tabulated Data from TCE:Soil Warburg Respirometry Studies.

Warburg Data for Unacclimated Chalmers Soil Supplemented with TCE from 2.5 Inch Depth. Table Dl.

Time, hrs.	End.	Glucose, 1,000 mg/l	TCE, 1,100 mg/l	TCE, 550 mg/l	TCE, 110 mg/1	TCE,a 55 mg/l	TCE, 55 mg/l
0.5	3	7.8	4	-2.34	-0.61	0.72	0.41
1.0	4.21	26.22	-5.08			0.29	S
1.5	8	2.6	~	-3.25	+1.52	0.07	0.73
	0.2	5.1	6	φ.	φ.	9.	0
		8.3	4.	6.		-2.14	-0.99
•	4.0	2.9	0			9.	-1.86
•	8.6	0.4	7	0.	.2	φ.	0.
•	9.5	01.6	-11.48	• 6		-2.52	• 6
	2.6	11.4	6.	4.	φ.		-2.82
•	0.7	28.4	7.3	-14.17	9.	0.	9.
•	9.9	32.4	.5	-15.48	4.	-5.06	.2
	2.3	3.1	-31.42	-17.16	. 7	.5	-6.70
5.	9.7	45.6	8.9	-20.29		0	0.4
7	8.4	41.8	-45.68	-23,72	7.4	-11.11	2.7
4.	07.5	44.0	6.1	4.		4.	2.6
•	1.2	40.1	-67.82	7.0	4.4	0	.5
φ	23.5	42.5	9.5	4.			3.8
<u>.</u>	32.1	40.3	٣.	5.6	7.2	φ,	6.5
5	36.6	36.9	0.8	4.		0	7.4
•	1.5	29.5	-107,15	.2	8.6		-25,30

Volume of soil used = 2ml Chalmers from 2.5 inch depth (2.70 g on dry wt basis).

Volume of liquid solution added = 1.0 ml

Table D1. Continued.

= Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. End.

Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

^aIndicates solution contained 2 ${
m mg/l}$ ammonia nitrogen.

Warburg Data for Acclimated Chalmers Soil Supplemented with TCE from 2.5 Inch Depth. Table D2.

ul 0 ₂	TCE, b 55 mg/l	0.92 -0.15 -0.22 0.11 0.69 0.78 1.26 1.31 2.43 3.42 4.94 5.73 5.73 6.95
Cumulative Oxygen Utilization, ul O ₂	TCE, a 55 mg/l	-1.21 -0.61 0.08 0.08 0.76 0.77 1.62 2.71 2.71 5.01 4.34
lative Oxygen	TCE, 55 mg/l	-0.27 -0.13 -0.12 -0.18 -0.18 -0.58 -1.95
Cumu	TCE, 110 mg/1	-2.35 -1.42 -0.63 -0.39 -0.46 -0.48 -0.43 -0.68 -0.41 -0.68
	Glucose, 500 mg/l	22.51 37.71 57.19 84.71 90.18 89.98 92.27 93.53 96.11 105.79 105.36 110.92 111.98 109.96
	End.	5.21 9.69 17.92 28.37 29.90 34.38 42.65 49.35 54.52 60.45 60.45 61.18 68.50 103.12 118.85 121.88
	Time, hrs.	0.5 1.0 1.0 2.5 3.5 4.5 7.5 10.0 12.5 12.5 24.5 33.75

Volume of soil used = 2 ml Chalmers from 2.5 inch depth from Column Cl2 (2.62 g on dry weight basis).

Volume of liquid solution added = 1.0 ml.

Table D2. Continued.

End. = Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

alndicates solution contained 1 mg/l ammonia nitrogen.

bindicates solution contained 2 mg/l ammonia nitrogen.

Warburg Data for Acclimated Chalmers Soil Supplemented with TCE from 15 Inch Depth. Table D3.

TCE, b 55 mg/l	•	-0.21	5			۲.	9	۳.	.5	4.	0	1.96	۳,	٦.	6.	9	5	9	.7	C
TCE,a 55 mg/l	-0.49	-0.04	\sim	$\overline{}$	\sim	0.29	4.	φ.	0.79	.2	9	1,37	1 85	1.75	6	6.	٦.	2.36	.2	~
TCE, 55 mg/l	-0.65	0.10	۲.	٤,	.2			6.	.2	9.	.7	1.82	6.	0		ω.			6.	
TCE, 110 mg/1	0.47	-0.64	-0.83	90.0	-0.31	1.27	0.31	0.40	0.19	-0.08	1.02	0.67	0.82	0.41	1,35	2.28	1.64	•	1.26	
Glucose, 500 mg/l	•	•	•	ä	4.	ж.	7.	7.	7	4.	φ.	73.09	5.	7.	α	.	•	8	9	8
End.	0	4.	4.	۳,	4.	4.	0.7	1.8	2.0	3.1	5.9	21.09	6.2	6.1	7.0	8.6	9.0	1.4	8.7	0.7
Time, hrs.	•	•	•	•	•	•	•	•	•	•	•	0.6	•	4.	•	4.	•	∞	0	4

Volume of soil used = 2 ml Chalmers from Column C12 (2.88 g on dry weight basis).

Volume of liquid solution added = 1.0 ml

Table D3. Continued.

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= Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. End

Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

aIndicates solution contained 1 mg/l ammonia nitrogen.

 $^{
m b}{
m Indicates}$ solution contained 2 mg/l ammonia nitrogen.

Warburg Data for Acclimated Chalmers Soil Supplemented with TCE from 31 Inch Depth. Table D4.

ul 02	TCE, b 55 mg/l	-0.65 -0.58 -0.58 -0.58 -0.95 -0.16 -0.16 -0.16 -0.16 -0.16 -0.16 -0.16 -0.16 -0.16
Cumulative Oxygen Utilization, ul O_2	TCE,a 55 mg/l	-0.37 -0.37 -0.46 0.41 -0.65 0.82 0.89 1.17 1.17 -0.91 -0.91 -0.94
lative Oxygen	TCE, 55 mg/l	-0.50 -0.10 -0.13 -0.14 -0.54 -0.94 -1.07 -1.05 -1.05 -1.05
Cumu	TCE, 110 mg/1	-2.61 -2.96 0.01 0.53 -1.12 -0.37 -0.03 -0.03 -0.16 -0.32 +0.32 +0.55
	Glucose, 500 mg/l	3.70 10.92 12.43 11.59 13.99 14.64 15.19 20.49 25.20 23.66 25.82 29.99 29.99 29.99
	End.	2.61 7.111 10.66 13.93 17.77 17.77 19.55 23.10 28.43 31.99 35.54 63.97 67.53
	Time, hrs.	0.0 1.0 2.1 2.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1

Volume of soil used = 2 ml Chalmers from Column Cl2 (2.96 g on dry weight basis). Volume of liquid solution added = 1.0 ml

Table D4. Continued.

= Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. End.

Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

^aIndicates solution contained 1 mg/l ammonia nitrogen.

bindicates solution contained 2 mg/l ammonia nitrogen.

Warburg Data for Acclimated Russell Soil Supplemented with TCE from 2.5 Inch Depth. Table D5.

			Сими	Cumulative Oxygen	Utilization,	, ul 0 ₂
Time, hrs.	End.	Glucose, 500 mg/l	TCE, 550 mg/l	TCE, 55 mg/l	TCE,a 55 mg/l	TCE, b 55 mg/l
İ	١ ٩	٩	۱		9	1
	•	ρ, c	-2.31	/ T O T		٠ ر
•		2.27	•	٦ ١	0.03	40
7		: m		99.0	•	1 (1
•	. 7	9		.2	0.11	3
.2	6.	.2	9		. 2	φ.
0.	6.	8.7	6	•	ω.	ω.
•	6.	8.7	-2.05	.3	•	
•	2.2	6.2	5	φ.	6.	.5
•	5.5	5.3	9	•	. 2	.2
•	6.5	0.0	2	ω.	0.	9.
•	1.0	3.4	•	.5	9.	.7
&	1.3	8.0	7	3,28	2.82	5
Ϊ:	6.9	6.2		4.	0.	.7
4.	2.1	6.9	. 2	6.	4.	6.
9	1.1	6.0	2.1	6.	. 2	φ.
j.	6.1	2.7	0.6	4.15		
δ.	9.0	6.7	.5		0	
•	9.0	6.1	-16.73		9.	
	2.6	03.6	ω.	4.16	5.06	
ф ж	2.6	03.8	-18.32		0	0.
6	4.8	02.2	0.5	6.	œ	φ.
;	6.3	02.5	0.7	٦.	.2	9.
34.0 96.0	93.80 95.30	100.95 101.56	-24.63 -22.99	-0.28 2.67	23° 00° 00°	2:83

Table D5. Continued.

(2.74 g on Volume of soil used = 2 ml Russell from Column 2.5 inch depth from Column R10. a dry weight basis).

Volume of liquid solution added = 1.0 ml.

= Oxygen utilization by soil with DI water as solution added, classified as andogenous metabolism. End.

Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

aIndicates solution contained 1 mg/l ammonia nitrogen.

bindicates solution contained 2 mg/l ammonia nitrogen.

Warburg Data for Acclimated Russell Soil Supplemented with TCE from 15 Inch Depth. Table D6.

ul 02	TCE, b 55 mg/l	-1.51 -0.089 -0.055 -0.19 -0.37 -0.68 -0.14 -0.68 -0.22 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33 -0.33
Utilization,	TCE,a 55 mg/l	1.51 -1.51 -0.33 -0.93 -0.16 -0.93 -0.93 -0.93 -0.94 -0.94 -0.94 -0.95 -0.95 -0.95 -0.95 -0.95 -0.95 -0.95 -0.95 -0.95 -0.95 -0.93
Cumulative Oxygen Utilization, ul	TCE, 55 mg/l	-1.03 -0.04 -0.24 -0.24 -0.24 -0.24 -0.21
Cumu	TCE, 110 mg/1	-1.51 -1.51 -1.53
	Glucose, 500 mg/l	-1.51 0.12 4.39 8.82 17.11 18.24 40.70 43.22 44.29 52.08 52.08 55.12 54.68 64.88 67.46 67.46
	End.	1.51 2.36 2.36 2.36 6.27 6.27 17.06 17.06 19.28 30.87 32.39 41.74 441.74 50.35 56.37
	Time, hrs.	0.5 1.0 1.5 2.0 2.0 3.0 4.0 6.0 10.0 113.0 113.0 126.0 33.0

Volume of soil used = 2 ml Russell from Column R10 (3.0 g on dry weight basis). Volume of liquid solution added = 1.0 ml.

Table D6. Continued.

End. = Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

aIndicates solution contained 1 mg/l ammonia nitrogen.

bindicates solution contained 2 mg/l ammonia nitrogen.

Warburg Data for Acclimated Russell Soil Supplemented with TCE from 31 Inch Depth. Table D7.

			Сими	lative Oxygen	Cumulative Oxygen Utilization, ul O ₂	ul 02
Time, hrs.	End.	Glucose, 500 mg/1	TCE, 110 mg/1	TCE, 55 mg/l	TCE, a 55 mg/l	TCE, b 55 mg/l
0.5 1.5 2.0 2.0 3.0 4.0 6.0 7.0 10.0 13.0 17.0 23.0	1.57 3.15 4.68 4.68 6.38 7.79 11.93 11.93 22.63 35.07 35.07	-0.79 1.54 2.140 2.47 2.18 11.68 11.22 11.22 11.90 22.10 21.73		-0.83 -0.61 -0.61 -0.84 -0.84 -0.68 -0.68 -0.91 -0.91	-0.93 -0.18 -0.18 -0.29 -0.31 -0.36 -0.36 -2.41 -2.41	1.053 1.053 1.053 1.053 1.033 1.3.85 1.3.85 1.888 1.888 1.52
•	4.6	-i	-9.48	•	0.26	-1.69

Volume of soil used = 2 ml Russell from Column R10 (3.12 g on dry weight basis).

Volume of liquid solution added = 1.0 ml.

Table D7. Continued.

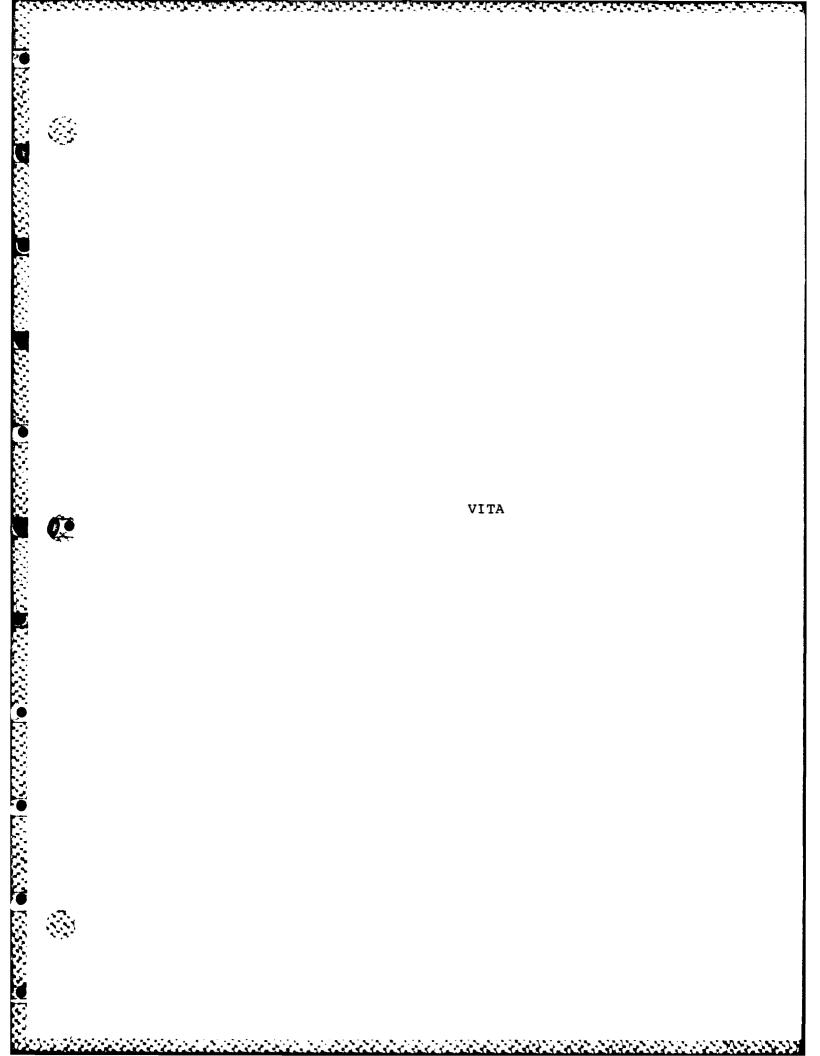
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= Oxygen utilization by soil with DI water as solution added, classified as endogenous metabolism. End.

Cumulative Oxygen Utilization = Oxygen utilization by soil over and above endogenous metabolism for metabolism of substrate indicated.

aIndicates solution contained 1 mg/l ammonia nitrogen.

 $^{
m b}$ Indicates solution contained 2 mg/l ammonia nitrogen.



VITA

Thomas Joseph Walker was born September 9, 1947 in Pascagoula, Mississippi to Bernard B. and Elsie J. Walker. He was married to Jane E. Hicks on June 7, 1969. They have three daughters, Jennifer, Rachel, and Katherine.

Mr. Walker was graduated from Our Lady of Victories High School in Pascagoula, Mississippi in May, 1965. He received his Bachelor of Science degree in Civil Engineering from Mississippi State University in January, 1970 where, upon graduation, he was commissioned a second lieutenant in the United States Air Force through ROTC. He earned his Master of Science degree in Sanitary Engineering from Mississippi State University in May 1971.

Mr. Walker began active duty service with the Air Force in July, 1971 and has served at Whiteman Air Force Base, Missouri; Osan Air Base, Korea; Reese Air Force Base, Texas; and Tyndall Air Force Base, Florida.

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